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DEGREE FINAL PROJECT

**Degree in Chemical Engineering**

# LIQUID-LIQUID SEPARATION OF NICKEL AND COBALT BY USING VERSATIC ACID 10 + PRIMENE 81-R IN SULPHATE MEDIUM

## Report and Annexes


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# Resum

Les operacions unitàries de transferència de massa reuneixen un conjunt finit de tècniques per separar espècies químiques. Aquestes es basen en l'aprofitament de diferents propietats físiques i químiques dels compostos involucrats.

Una d'aquestes operacions és l'extracció líquid-líquid, que està relacionada amb la solubilitat i la densitat. El seu ús sol ser de baix cost i fàcil d'implementar.

Actualment, l'extracció líquid-líquid avança un pas més amb l'ús de extractants orgànics selectius que permeten extraccions més específiques. El seu poder rau en l'aparició de certes reaccions químiques que afavoreixen la separació líquid-líquid tradicional.

Dins de la gran varietat de extractants orgànics es troben certs tipus d'amines i àcids. Barrejats, conformen una solució orgànica tal que permet captar una part important de l'espècie objectiu si s'escullen bé les espècies.

El present projecte té com a objectiu estudiar l'eficàcia d'una barreja d'àcid versátic 10 + PRIMENE 81-R (amina primària) per separar el níquel aquós i el cobalt en diferents condicions. La fase orgànica es pretén que sigui neutra i, per tant, els cations s'alliberin sense generar protons al medi.

Per provar l'efectivitat del extractant es fan diversos assaigs que, tot modificant diverses variables d'extracció del procés, afecten la concentració de la fase orgànica, la concentració de sal a la fase aquosa i la concentració inicial de metalls.

A partir dels resultats, certs models poden ser construïts a fi de predir el comportament del extractant en unes condicions particulars.

Eventualment, es dissenya la simulació d'un procés a contracorrent a partir de dades empíriques que pretén donar una visió aproximada de com funcionaràn aquests estudis en una situació potser extrapolable a la indústria.

# Resumen

Las operaciones unitarias de transferencia de masa reúnen un conjunto finito de técnicas para separar especies químicas. Estas se basan en el aprovechamiento de diferentes propiedades físicas y químicas de los compuestos involucrados.

Una de estas operaciones es la extracción líquido-líquido, relacionada con la solubilidad y la densidad, su uso suele ser de bajo coste y de fácil uso.

Hoy en día, la extracción líquido-líquido avanza un paso más con el uso de extractantes orgánicos selectivos que permiten extracciones más específicas. Su poder radica en la aparición de ciertas reacciones que favorecen la transferencia de masa.

Dentro de la enorme variedad de extractantes orgánicos se encuentran ciertos tipos de aminas y ácidos. Mezclados, conforman una solución orgánica tal que permite captar una parte importante (si se escogen bien los extractantes) de la especie objetivo.

El presente proyecto tiene como objetivo estudiar la eficacia de una mezcla de ácido versático 10 + PRIMENE 81-R (amina primaria) para separar el níquel acuoso y el cobalto en diferentes condiciones. La fase orgánica se pretende que sea neutra y, por tanto, que los cationes se liberen sin generar protones en el medio.

Para probar la efectividad del extractante, se hacen varios ensayos que modifican varias variables de extracción del proceso. Estos cambios afectan la concentración de la fase orgánica, la concentración de sal en la fase acuosa y la concentración inicial de metales.

A partir de los resultados, ciertos modelos pueden ser construídos con objeto de predecir el comportamiento del extractante en unas condiciones particulares.

Eventualmente, se diseña la simulación de un proceso a contracorriente a partir de datos empíricos que dan una visión aproximada de cómo funcionarán estos estudios en una situación encontrada, quizá, en industria.

# Abstract

Unit mass transfer operations gather lots of different techniques to separate compounds. These, are based on the exploiment of different physical and chemical properties of the compounds involved.

One of these operations is liquid-liquid extraction, related with solubilities and densities, making it a cheap and easy way to separate different species.

Nowadays, liquid-liquid extraction goes a step further with the usage of selective organic extractants which permit more specific extractions. Its power bases on the engagement of certain reactions.

Within the huge variety of organic extractants are found certain types of amines and acids. Mixed, they conform precise organic solutions that, applied correctly, will retain the target specie.

The present project aims to study how good a mixture of versatic acid 10 + PRIMENE 81-R (primary amine) is, in order to separate aqueous nickel and cobalt in different conditions. The organic phase is meant to be neutral and thus, cations are reatined without releasing protons to the medium.

To test the extractant effectiveness, various essays are made modifying several process extraction variables. These changes affect the organic phase concentration, the concentration of salt in the aqueous phase and the initial concentration of metals.

From the results, some models may be constructed and hence, the behaviour may be predicted in these particular conditions.

Eventually, the simulation of a countercurrent process is designed from empiric data giving a view of how would these studies work in a situation commonly found in industry.

# Acknowledgements

First of all I would like to acknowledge the attention and support of my laboratory partners because, without them and their advice I might not be able to face the challenge that this project represents as I did. Some of them are from different cultures, but with all our combined efforts and the desire of do things nicely, the experience has been very pleasant.

Also, I express my gratitude to the professors Antonio Gámez, Agustí Fortuny, Maria Teresa Coll and Maria Antonia Majó that have helped me and led me through all this apprenticeship.

I could not forget all my collegues and professors from university and their efforts to pull us all into the right direction. This challenge has become an enjoyable trip because of them.

Likewise, my college buddies with whom I have grown through these years and have developed a common project never seen before in Catalonia, the creation of a Student Chapter related to the American Institute of Chemical Engineers, giving the chance of take contact with thousands of students and professionals worldwide.

And...

Also to you for reading this project in which I have put my best effort. I hope you enjoy it as much as me.

# Glossary

*This part includes several simbols, signs and abbreviations which appear throughout the project to avoid repetition.*

Table 1: Glossary

| | |
|---|---|
| 81R | PRIMENE 81R |
| aq | Aqueous |
| Co | Cobalt |
| D | Distribution ratio |
| E | Extract |
| Ext. | Extraction |
| Extnt. | Extractant |
| F | Feed |
| H | Proton |
| HA | Acid |
| ind | Individual |
| ini | Initial |
| $K_{ext}$ | Extraction constant |
| liq-liq | liquid-liquid extraction |
| M | Molarity |
| Me | Metal |
| MeA2 | Organometalic compund |
| mix | Mixed |

| | |
|---|---|
| Na | Sodium |
| Ni | Nickel |
| OH | Hydroxide |
| org | Organic |
| pH | pH |
| R | Substituent group |
| RR | Raffinate |
| r | Phase relationship |
| R2HN | Secondary amine |
| R3N | Tertiary amine |
| RH2N | Primary amine |
| S | Solvent |
| SO4 | Sulphate |
| Stp | Stripping |
| T | Temperature |
| t | Time |
| V | Volume |
| v10 | Versatic acid 10 |
| β | Separation ratio |
| δ | Compound formation constant |
| ω | Volumetric flux |

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# REPORT

# 1. Preface

## 1.2. Project origins

In the second half of the twentieth century, several important manufacturers of chemical products started to develope new brand reagents. These had particular capabilities to exploit and they were applied in some processes related to paint production or additives for other reagents synthesis.

It was seen that these products combined with others were able to retain species dissolved into water but, going even further than the traditional liquid-liquid extraction, these processes involved also a chemical reaction which was specially selective with some solutes.

The acknowledgement of its potential gave place to the synthesis of new extractants, more specific for each kind of solute and with it, several species that were particularly hard to separate started to be treated with easier techniques that made the task cheaper.

## 1.3. Motivation

For those students who are eco-friendly and aim to more sustainable processes, this kind of project grants the opportunity to enhance the knowledge of mass unit transfer operations and chemical-reaction engineering. Also, being an experimental project, it is particularly benefitial to improve laboratory and analytical skills.

## 1.4. Previous requirements

As mentioned, it is essential to have some notion of unit mass transfer operations in order to have criterion enough when the data are managed. Also, chemical-reaction engineering when the models are created is vital. Without these tools, it would be much harder to do the project and it would be considered as a severe lack.

# 2. Introduction

To obtain and purify transition metals, metallurgic industry uses different techniques related to chemical and physical processes. Amongst the variety of operations used in hydrometallurgy, where sometimes a metal is found dissolved into water and it has to be treated, there is a technique that may separate metals by contact and agitation.

Liquid-liquid extraction is a unit mass transfer operation where 2 or more different phases, immiscible each other, come in contact sharing a certain specie dissolved. Its potential lies in how good the carrying phase is chosen and also other factors, such how the system is adapted to the surroundings (operating conditions). Thus, depending on the operating conditions, the splitting will benefit more or less the phase meant to perceive the target solute.

Thoughout this project, selective liquid-liquid extraction will be studied having a medium rich in sulphates by using a mixture of extractants (PRIMENE 81-R + versatic acid 10).

## 2.2. Project goals

For each unit mass transfer operation there are some variables involved which play a key role so it is a major factor to be careful with the operating conditions. In fact, a slight change in the aqueous or the organic phase contitions may delay or even stop the process. Are the factors like pH, the surrounding temperature, the extractant concentration or even the solute, are some of the most common variables to consider.

Having this in mind, the next step is carry out the experiments that will conform the required set of data necessary to construct a countercurrent process and generate the reaction models. Obviously, depending on the results, the models will follow a certain path and some studies would start from the best results of the previous ones, always aiming to separate the metals and not only the success of the extraction.

This will lead the project, as mentioned, to a multi-stage countercurrent process that will be compared with the results from isotherms. The error between both set of data will be compared in order to determine how accurate the model is and, more importantly, how the mathematic model with a set of hypothesis related, deviates from a real life.

## 2.3. Project depth

To start with, the current problem must be correctly defined. Holding an aqueous phase which needs to be treated, it is found that a various techniques would do the work. However, it has been stablished that the main technique used will be selective liquid-liquid extraction so, first of all, the determination of a good extractant is essential.

As an additional condition, it has been decided that oxymes[1] will be not used.

Now, the main targets are: examine the best proportion of amine and acid, determine the best dilution of the chosen extractant, check how some variations may change it, construct the isotherms and elaborate a countercurrent process.

Moreover, from individual data of nickel and cobalt, the constant of extraction can be isolated and the model of extraction constructed.

Due to the features of PRIMENE 81-R which has a short chain, the reusage of the organic phase, which would be also an interesting aspect to study, cannot be considered.

[1] An oxime is a chemical compund which belongs to imines and usually is generated by the reaction of ketones and may retain certain types of metal.

# 3. Theoretical part

## 3.2. STUDIED METALS AND PROPERTIES

### 3.2.1. NICKEL AND COBALT SEPARATION

Due to their features, nickel and cobalt are separated easily from the rest of metals but, unfortunately, they are hard to separate each other because of their chemical and physical similarities.

However, there is a set of metallurgical techniques that may do this task. Depending on their nature, these techniques are sorted as pyrometallurgical, electrometallurgical and hydrometallurgical. These may be combined each other in order to obtain greater results reducing the overall cost.

In industry, it is found the usage of pyrometalurgicall and hydrometallurgical techniques combined in major or minor proportion to enhance the processes but, at the same time maximize the benefits and minimize the contamination.

Traditionally, liquid-liquid extraction was used most of times with rare and valuable metals. Nowadays, due to the current wide variety of extractants and their properties, this technique may be applied to a wider spectrum of metals.

Another important consideration is that selective liquid-liquid extraction is underway. It is currently being developed from combining different existant extractants in order to create new organic phases much more adequate for each type of aqueous solution to treat.

### 3.2.2. NICKEL

Nickel is a wide extended metal which represents the 0,02% in mass of the total amount of the Earth's crust. Unfortunately, it's very hard to find places where the ore can be found so mining operations are quite uncommon.

The main kinds of ore which contain nickel are the following ones:

Garnierite ((Ni, Mg) H2SO4)

Nickeline (AsNi)

Millerite (NiS)

Pentlandite (SNi2·2SFe)

Now, moving on to some of its properties,

Table 2. Nickel properties

| Property | Nickel |
|---|---|
| Symbol | Ni |
| Atomic number | 28 |
| Atomic weight | 58,71 (g/mol) |
| Stable oxidation numbers | +2 and +3 |
| Electronic structure | Ar $3d^8 4s^2$ |
| Acid/Basic properties | Basic |
| Crystal structure | Face-centered cubic |
| Density | 8,902 (g/mL) |
| Atomic volume | 6,6 |
| Ionitation potential | 7,633 eV |
| Melting point | 1453 $^oC$ |
| Boiling point | 2730 $^oC$ |
| Specific heat | 0,105 cal/(g·$^oC$) |

#### 3.2.2.1. PRODUCTS

Salts from nickel are usually found as divalent salts, trivalents are quite hard to find. Some of these show a grennish tone and others form hydrates. Amongst the different nickel compounds are found:

- Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$)

- Nickel's chloride hexahydrate ($NiCl_2 \cdot 6H_2O$)

- Nickel's sulphate heptahydrate ($NiSO_4 \cdot 7H_2O$)

- Oxides and hydroxides (NiO), $Ni(OH)_2$

- Complexes

#### 3.2.2.2. USES

There are some metals which gather good features remaining pure, such as coper. On the other hand there are some that require some aspect to be enhanced. Adding some traces or a great proportion of nickel to the pure metal, some alloys are created. These may be less brittle, gain electromagnetic capacity or more corrossion resistance. Nicrom IV and Permalloy are just 2 examples inside the huge variety of current Ni alloys.

### 3.2.3. COBALT

Cobalt is a slow-reacting transition metal with a blue tone. It has several ferromagnetic, thermic and electric properties and shares some similarities with nickel.

The main kinds of ore which contain nickel are the following ones:

- Asbolane ($(Ni,Co)_{2-x}Mn^{4+}(O,OH)_4 \cdot nH_2O$)

- Cobaltine (CoAsS)

- Eritite ($Co_3(AsO_4)_2 \cdot 8H_2O$)

- Heterogenite (CoOOH)

- Smaltite ($CoAs_2$)

In the following table the most relevant properties of cobalt are shown:

Table 3. Cobalt properties

| Property | Cobalt |
|---|---|
| Symbol | Co |
| Atomic number | 27 |
| Atomic weight | 58,94 (g/mol) |
| Stable oxidation numbers | 2+ and +3 |
| Electronic estructure | $3d^7 4s^2$ |
| Acid/Basic properties | Amphoteric |
| Crystal structure | Hexagonal |
| Density | 8,7 (g/mL) |
| Atomic volume | 6,77 |
| Ionitation potential | 7,86 eV |
| Melting point | 1492 $^oC$ |
| Boiling point | 2900 $^oC$ |
| Specific heat | 0,1 cal/(g·$^oC$) |

#### 3.2.3.1. PRODUCTS

From cobalt are found various species that may be divalent or trivalent. Amongst the different cobalt compounds are found:

- Cobalt chloride (II) ($CoCl_2$)

- Cobalt sulphure (II) (CoS)

- Cobalt sulphate (II) heptahydrate ($CoSO_4 \cdot 7H_2O$)

- Oxides and hydroxides (CoO, $Co_2O_3$) ($Co(OH)_2$)

#### 3.2.3.2. USES

Cobalt may be found in superalloys and it is also corrosion and wear-resistant, also has a good temperature stability. It may be found in batteries, as a catalyst or even as a pigment so it is quite frequent in industry.

## 3.3. LIQUID-LIQUID EXTRACTION

### 3.3.1. General aspects and configurations

As unit mass transfer operation, liquid-liquid extraction bases its potential on retaining one or more species that previously were dissolved differently. By doing this, a target set of materials may be moved, splitted, concentrated or diluted after a certain time of contact.

These target species are called “solute” and they may be found in an aqueous solution just as happens in the current study. However, there are more options available within liquid-liquid extraction, like amalgamation which uses mercury.

Traditionally, the different mass currents were named as:

· Solvent (S): The (organic) flow that will perceive a part of solute.

· Feed (F): The (aqueous) flow that initially holds solute.

· Extract (E): The (organic) flow that has already perceived the solute

· Raffinate (RR): The (aqueous) that has lost a part of its solute.

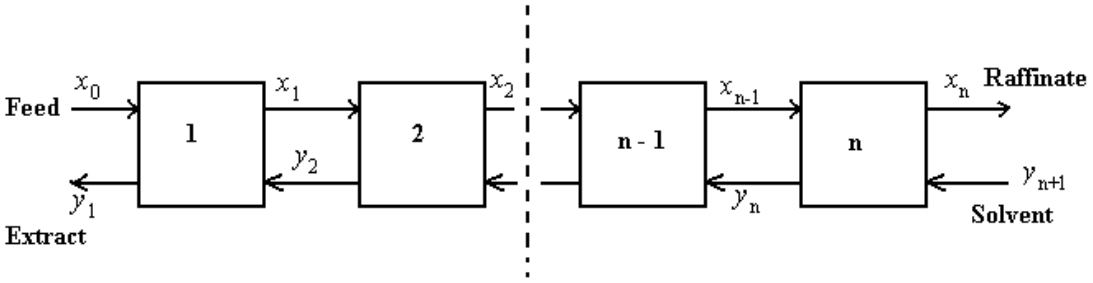


Fig 1: Countercurrent liq-liq extraction scheme

Currently, the usage of specific organic extractants makes the task of metal separation and recovering easier and more sustainable.

Nevertheless, it is convenient that both phases are inmiscible so a good solute distribution may be achieved and avoid undesired side effects.

Moreover, an additional operation may be applied in order to separate and recover the solute from the extract, this is called stripping. It takes place when a new aqueous phase comes in contact with the organic phase. It is very interesting to apply this technique in order to separate the solute from the organic and leave it free of solute to its reusage, if it is possible.

Also, once the stripping has been completed, it is important to do something else to restore as much as possible the extractant initial features. This is achieved by means of clearance or washing as long as it was worthy. Poor performance rates suggest that the organic cannot be used anymore.

On the one hand, the extraction process may be achieved by means of various ways. These are:

· Non-continuous processes: Also called “Batch”, works achieving a theoretical equilibrium or a desired concentration of certain specie. The whole process is hold by a same structure which does not present any special change in each part of the system as long it had been stirred properly.

· Continuous process: Here, it is totally the opposite. The reagents flow from a certain point of the system to another. During this movement, they experience different changes and, more importantly, the surrounding conditions may also vary. Usually, it is stablished a concentration gradient throughout their route.

On the other hand, there are geometrical considerations which give place to:

· Stage-by-stage contact: In this case, the entire system is divided in several trays or stages where a theoretical equilibrium is achieved. This sounds pretty like a non-continous process but there is a subtle difference, it is a dynamic system where the reagents are constantly in movement. These reach a certain equilibrium and then move on to another stage where the equilibrium is different.

· Packed contact: These, unlike the previous mentioned, are filled with some kind of bodies and materials that ensure a continuous contact throughout the system. In this case, there is not equilibrium reached within the “infinite trays” that shape the system but there is a set of thermodynamic expressions that lead the process to react.

Within stage-by-stage variety, there are different methods acording to the requirements:

· Direct contact: This method is opposite to the previous one. Here raffinate and extract enter through the same place. It involves normally a smaller driving force so it gives worse results than countercurrent.

· Countercurrent contact: In case the processtakes place in an extraction column. This one would aim to force the contact through the column in a certain way so the raffinate and the extract leave the column oppositely. This means that the raffinate enters where the extract leaves.

· Crossed-stage contact: Here, fresh extractant enters in each stage. When an extractant has a low carrying capacity, it is frequently the most interesting way to separate the species.

Obviously, the previous methods are based on theoretical models which, in real life, are combined each other to give better results depending on their kinetics and other aspects. Some real devices that may do the liquid-liquid extraction are:

· Contact columns: These were previously mentioned and depending on the operation it is pretty hard to predict its behaviour accurately with only thermodynamic relationships and pressure, motion and heat loss equations.

· Mixer-settlers: These combine agitated tanks and decanters and might need some centrifugal action in order to separate phases which similar density.

Fortunately, all these devices are usually pretty cheap, their low cost, in terms of energy, and the possibility of recovering and reusage of the organic phase makes liquid-liquid extraction very attractive. However, it is very important to use the technique correctly because emulsions may be formed and some organic might solubilize into the aqueous putting in trouble the entire process.

### 3.3.2. LIQUID-LIQUID PRINCIPLES

- Extraction performance

It is the percentage of the total amount of metal extracted of the organic phase $|Me|_{org}$ divided by the metal initially found in the aqueous phase $|Me|_{aq}$, that is to say:

$$\%E = \frac{|Me|_{org}}{|Me|_{aq}} * 100 \quad (1)$$

- Stripping performance

It is the percentage of the total amount of metal recovered from the organic phase by the new aqueous phase $|Me|_{aq}$ divided by the overall metal contained by the organic phase $|Me|_{org}$:

$$\%S = \frac{|Me|_{aq}}{|Me|_{org}} * 100 \quad (2)$$

Now, since the concentration of the organic cannot be known, it is just to substract the $|Me|_{aq}$ from the $|Me|_{ini}$:

$$|Me|_{org} = |Me|_{ini} - |Me|_{aq} \quad (3)$$

The ratio of the extraction percentages allows to compare the extraction conditions. For instance, comparing the extractions of a metal when it is found mixed with something else (another solute) or not, and varying the concentrations of the extractant used.

By doing this, the influence of a second specie may be quantified. A simple relationship as the one shown below can give some advice of how affects the addition of more species:

$$\%_{variation} = \frac{|Me|_{mix}}{|Me|_{ind}} \quad (4)$$

Obviously, the only variable here is the solute. The rest of terms have to remain as fixed much as possible.

The distribution of any solute is, as mentioned, usually affected by the presence of one or various species. These may interfere during the extraction or interact in a certain way with the solute. Directly or indirectly, severe changes may be observed, for instance, when any other specie that affects the solute directly is modified by a third specie. Depending on how the interaction occurs, in some cases, the extraction is boosted, delayed or even stopped.

It is known as extraction constant the equilibrium constant of the global reaction of distribution. It is usually found in literature as $K_{ext}$ and, for a reaction of extraction which involves an ionic specie of metal and a cationic organic phase, the reaction occurs as shown below.

$$aMe^{n+} + b\overline{HA} \leftrightarrow cH^{+} + dA_nMe \quad (5)$$

Where:

$Me^{n+}$ is any solute (metal in the current case).

HA is the abbreviation of the organic acid.

a, b, c, d are stoichiometric coefficients.

And sorting the terms, the extraction constant is isolated:

$$K_{ext}\frac{|H^+|^c * |\overline{AMe}|^d}{|Me^{n+}|^a * |\overline{HA}|^b} \quad (6)$$

Sometimes, depending on what kind of extractant is applied, the kinetics are very slow. The distribution ratio, expressed as D, can be used if the reaction is sufficiently time consuming to take place, however certain kinetic considerations must be applied to understandbetter the operation of the studied system.

$$D_{Me} = \frac{\sum\overline{|Me|_{org}}}{\sum|Me|_{aq}} \quad (7)$$

Another concept known as the ratio of separation is introduced in case that the aqueous phase contains one or more susceptible species extracted. The ratio of separation, expressed as β, relates the coefficients of the two elements.

B may be expressed as the distribution ratio of the specie that has been separated the most divided by the one that less extracted is.

$$\beta = \frac{D_{Me(max)}}{D_{Me(min)}} \quad (8)$$

Then, the different β are plotted and displayed in order to find the maximum. This point shows the concentration that ensures a higher separation for a certain experiment.

On the other hand, the volumes of the phases determined the material balance in the extraction process considering that the volumes of the phases before and after the extraction that the initially extracted phase does not contain any solute. The balance of matter is shown below.

$$|Me|_{aqini} * V_{aq} = |Me|_{aq} * V_{aq} + |Me|_{org} * V_{org} \quad (9)$$

Being:

$V_{aq}$ = Volume of the aqueous phase

$V_{or}$ = Volume of the organic phase

$|Me|_{aqini}$ = Initial concentration of the solute in the aqueous phase

$|Me|_{aq}$ = Concentration of the solute in the aqueous phase when the equilibrium is reached

$|Me|_{or}$ = Concentration of the solute in the organic phase when the equilibrium is reached

- Phase relationship

Also, another concept to consider is the phase relationship, expressed as "r", which can be related to the mass balances, considering their volume as constant at any time.

It is defined as the volume of the aqueous phase divided by the volume the organic phase. In the same way, in a continuous system it can be expressed not as volumes but as flows, considering the same previous hypothesis saying that the flows are constant.

$$r = \frac{V_{aq}}{V_{org}} = \frac{\dot{\omega}_{aq}}{\dot{\omega}_{org}} \quad (10)$$

This concept will be especially interesting during the countercurrent process because the splitting depends directly of the volume relating the mass balances.

### 3.3.3. LIQUID-LIQUID USAGE

This mass transfer unit operation is used to separate components into a liquid solution. Particularly, its usage is meant for:

· Non-volatile reagents.

· Those which their boling points are pretty similar. If that was not the case, maybe other operations such as distillation might be considered.

· Following the previous point suggestion, liquid-liquid extraction is also used when the compounds are sensitive to their boiling temperatures.

· When the target compounds are less volatile and they are found in small amounts.

· Concentrate phases.

### 3.3.4. LIQUID-LIQUID COMPONENTS

#### 3.3.4.1. THE AQUEOUS PHASE

The aqueous phase is the one that normally contains the solute dissolved. There are various factors that may have a particular impact on the solution properties and the overall extraction process:

- Solutes concentration: This may affect the extraction process by causing interferences. It may give place to the organic phase does not work properly (solute is not extracted) because if the species are similar enogh, the various solutes may become competitors or may increase the density, boosting the separation.
- Salty agents concentration: Salty agents are, most of times, inorganic salts from acids or other salty compounds. These may also improve the separation of the phases due to the increase of density in the aqueous phase or delay it if the species formed interfere with the global extraction.
- The pH: The pH measurement gives important information about the formation of species affected by the presence of $H^+$ and $OH^-$. In certain ranges of pH just some types of ions are formed and these, at the same time, might have some impact on the conditions of the experiment. In fact, the pH value is normally related with complexes formation into the aqueous phase that may boost or delay the extraction of a certain solute.

In the current project, the usage of a neutral extractant aims to set the pH, making the process more stable. However, a pH-meter will be used in order to guarantee this statement.

The aqueous phases chosen to do the experiments are generated from the following stock solutions:

Table 4: Aqueous stock solutions

| ID | Ni (mg/L) | Co (mg/L) | $SO_4$ (M) |
|---|---|---|---|
| A.1 | 5000 | 500 | 0,09 |
| A.2 | 5000 | 500 | 0,50 |
| A.3 | 5000 | 500 | 1,00 |
| A.4 | 5000 | 0 | 0,50 |
| A.5 | 5000 | 2000 | 0,50 |

From the different combinations are synthesized lots of different aqueous solutions. All of them are located within the previous ranges of concentration, being 5000 mg/L of nickel and 2000 mg/L (more likely 500) the maximum concentration of metals.

#### 3.3.4.2. THE ORGANIC PHASE

During the extraction process, the organic phase, that has to be immiscible into the aquous and non-dissociating, has to extract and retain the metals from the aqueous phase.

However, it is very important to have in mind that the organic phase is typically a mixture of various reagents which may be an extracting agent, a diluent or a modificator. Hence, the organic phase design must consider that this mixture fulfill the main requirements.

In general terms, the organic phase components are sorted as:

- The extractant agent: Which is the key component and presents some kind of affinity for some of the target species meant to be extracted. Normally it works generating complexes with the target solute. This extractant agent is classified according to its characteristics such as its shape, its functional groups, number of carbons or its extraction mechanism, for instance.

Also, as mentioned before, this extractant agent is usually mixed with other reagents to enhance its capabilities so in literature, most of organic phases are designed applying this principle.

The main properties that must have any extractant agent are the following ones:

· Immiscibility: This property is very important due to the higher degree of recovering of the extractant so the loss of organic in the raffinate decreases.

· Selectivity: As the ability which has the extractant to extract certain specie, is the term which makes the difference between a simple liquid-liquid extraction and the current one. Having a high selectivity, the extractant reacts mostly with the target specie. In the current project it is needed an organic capable to retain one of both metals. Ideally, the target metal gives place to a very high extraction whilst the other remains dissolved into the aqueous phase.

· Carrying capacity: It refers to the maximum concentration of the target metal dissolved into the organic. This feature may be modified in concordance to (e.g.) pH, the present of salts or temperature.

· Distribution ratio: As the relationship between the metal concentration of the organic phase and the one from the aqueous. It is aimed then that the number was high so the process succeeds as much as possible.

· Recoverability: It is quite interesting to recover a part of the organic since it can be used again mixing it with fresh organic or used afterwards. By doing this, the processes are cheaper and more sustainable. However, the recovering is not unlimited. So it is necessary to regenerate the organic with fresh extractant regularly after various cycles of extraction.

· Density: It is very important to have a certain density difference so the phases separate by means of gravity. The higher the difference is the faster they separate after agitation.

· Surface tension: As surface tension rises, coalescence makes faster the formation of the phases.

· Viscosity: It is convenient to have a low viscosity because it boosts the mass transfer, the phases separation and its handling.

· Chemical stability: It is meant to work in certain conditions of temperature, pressure and concentration. However, by choosing some kind of extractant agent resistant to slight changes on the operating conditions, it may gain stability, and also that will not react with other species but those of interest.

· Cost: Depending on the benefit obtained of doing this process it will be more or less convenient the usage of the species that conform the organic.

·Safety and environmental impact: It is very common to find extractants not highly dangerous so they can be managed without very special security devices. These can be dumped into special containers so it is vital to manage them with extreme care once they become organic waste.

- The diluent: It is used normally to reduce the extractant agent viscosity and promote the aqueous/organic contact. During the process, it is normally inert although it may participate positively, increasing the separation. In fact, a high extractant concentration does not ensures a high separation rate if the contact is not that good.

As diluent, some reagents might be considered to be used, for example: Kerosene, Exxol D100, Xilene or Sovesso.

However, it cannot be choosen that lightly and must gather several conditions, such as follow:

· The extractant agent must be soluble into the diluent. Obviously, it has to accomplish this point in order to obtain an organic solution to work with.

· Low solubility into water. Following the previous reasoning, it has to be non-soluble into water (ideally) to lose as little as possible volume of reaction and also ensure the mass balances.

· Low viscosity: To make faster the separation and handling (same as the extractant).

· Chemical stability: In this case it is particularly interesting that the diluent will not interfere in any way because its role it is just improve physical aspects of the organic phase.

- The modificator: Sometimes, an extra specie is added to enhance the organic phase extractive properties. These may be able of:

· Improve the solubility of the extractant agent into the organic phase.

· Enhance the solubility of the complexes formed with the metal.

· Optimize the phase separation.

· Upgrade the overall extraction.

### 3.3.5. EXTRACTIVE METHODS

Versatic acid 10 or neodecanoic acid is a reagent formed by the mixture of several organic acids which share a same molecular formula ($C_{10}H_{20}O_2$). As an acid, it will be represented as "HA". Once versatic 10 is in contact with an aqueous phase that contains dissolved metals, these may be exchanged by protons.

The reaction that occurs is shown below:

$$Me^{2+} + \overline{nHA} \leftrightarrow \overline{A_nMe} + nH^+ \quad (11)$$

Whilst liquid-liquid extraction is taking place, the protons in the aqueous phase move to the right side of the stoichiometric equation, first delaying and eventually stopping the extraction once the equilibrium has been reached.

To avoid this, some kind of inorganic base may be introduced into the system to neutralize the protons and keep going with the extraction. However, it is seen that generates certain problems in continuous processes so, in this situation, it is much more convenient to generate a neutral organic phase (explained in 3.5).

This base, the amine, can be primary, secondary, tertiary or quaternary depending on the number of substitutions. In literature these compounds are found as:

Table 5: Types of amines

| Type | Abbreviation |
|---|---|
| Primary | RH2N |
| Secondary | R2HN |
| Tertiary | R3N |
| Quaternary | R4N+X- |

Another curious fact is that primary, secondary and tertiary amines require a previous protonation to work as ionic extractant. This protonation may be expressed as follows:

$$\overline{RH_2N} + H^+A^- \leftrightarrow \overline{RH_2NH^+A^-} \quad (12)$$

for a primary amine,

$$\overline{R_2HN} + H^+A^- \leftrightarrow \overline{R_2HNH^+A^-} \quad (13)$$

for a secondary amine,

$$\overline{R_3N} + H^+A^- \leftrightarrow \overline{R_3NH^+A^-} \quad (14)$$

for a tertiary amine.

Referring to extraction, it consists in an ionic exchange which responds to the following shape:

$$X\overline{R_XH_XNH^+A^-} + XSalt_X^{X-} + XMe^{X+} \leftrightarrow \overline{(RH_2NH)_XXSalt_X^{X-}} + XA^- \quad (15)$$

According to the type of amine combined with the acid (neodecanoic), the degree of protonation will vary more or less giving place to very different results.

Following the previous relation for primary amines, mentioned before, the acid may be substituted by $\overline{HA}$ which corresponds to the general stoichiometry.

$$\overline{HA} + \overline{RH_2N} \leftrightarrow \overline{RH_2H^+A^-} \quad (16)$$

On the other hand, referring to the extraction, including sulphates as salt, the stoichiometry may be expressed as:

$$2\overline{RH_2H^+A^-} + Me^{2+} + {SO_4}^{2-} \leftrightarrow \overline{(RH_2H^+)_2SO^{2-}} + \overline{MeA_2} \quad (17)$$

Having a look to the reaction above it is seen that some free sulphates from the aqueous phase become part of the amine. This new specie, takes a bifunctional role being anionic and cationic thanks to the presence of the amine and the acid, respectively.

## 3.4. MAIN HYPOTHESES

Due to the changes that the system may suffer and other factors, some hypotheses are taken to do the study more feasible. These are:

- Volumes added to the system are always constant, although in reality they are not losing the experimental extraction process from these volumes.
- The temperature of the systems will always be considered the same (20°C±5) and the pressure as 1 atm.

- The optimum agitation time is considered to be the total time of 20 minutes in which the systems are in agitation.
- The time required to do the separation before the extraction is about 20 minutes (at least). For stripping, until the aqueous phase becomes clear.
- The stoichiometry initially will be assumed as 2, changing it if necessary.

## 3.5. THE EXTRACTANT

Currently, there are different kinds of extractants. They are sorted according to their structure, the species they extract, their extracting mechanism and so on.

In terms of the extracted specie's nature, extractants are classified as:

· Cationic extractants: These may be of chelate type forming chleates when they combine themselves with metal ions (these have an elevated selectivity) or organic acid that act exchanging protons for metal ions.

· Anionic extractants: These normally work by ionic association. Being mostly primary, secondary and tertiary, they need a protonation in order to be able to work as an anionic extractant.

· Neutral extractants: Known also as "solvating", induce a solvating effect on certain metal complexes swaping hydration areas. This makes the complexes insoluble into water so the organic phase mass remain almost constant. By means of its usage some cationic species can be extracted, which mostly are phosphorous compounds.

### 3.5.1. THE ORGANIC PHASE PROPOSED

The current study aims to separate successfully cobalt from nickel by using a mixture of reagents that generates an extractant. This main purpouse is achieved by removing cobalt from the aqueous phase so there is a separation. It is required then a good selectivity in order to achieve this requirement and there are, as mentioned, several ways to do it.

However, there are more factors that may be considered during the selection and may have reference to how easily the solute extracted can be discharged into another aqueous phase (especially interesting when the solute is some kind of precious metal, for instance), how easily the extractant can be restored and reused, be stable and immiscible into the aqueous phace how it responds to safety statements and evironmental factor, how it avoids the emulsions creation and how affordable would be its implementation in the corrent project.

From the convergence of all these factors quantified, some kind of function may be generated and the product closer to its optimal point would be chosen.

To choose an extractant, some amines have been selected as candidates. Combined with versatic acid 10 (fixed in this case) are obtained various results that give some advice of how good the extraction and the separation are.

If these figures show that there is not any significant extraction in a particular mixture, this will be discarded as shown in chapter 4.

### 3.5.2. CARACTERISTICS OF THE CHOSEN ORGANIC COMPOUNDS

- PRIMENE 81-R: It is a mixture of isomeric amines in the C12-14 range. Being an aliphatic amine with highly branched alkyl chains, its amino nitrogen atom is linked to a tertiary carbon to give the t-alkyl grouping.

Just as happens to other products of PRIMENE series like JMT or TOA, they have unique chemical and physical specs, being especially resistant to oxidation, and with fluidity and viscosity particularly low in a wide range of temperature, also highly soluble into petroleum hydrocarbons.

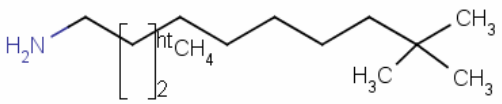


Fig 2: PRIMENE 81R molecule

It is normally observed that other substances (mixtures) synthesised from this amine gather some of these properties. The manufacturer claims that it has particular interest on the salts of organic acids, phenols, complex inorganic acids based on heavy metals, and other compounds that show unusually low solubility in oils and hydrocarbon solvents.

Table 6: PRIMENE 81R properties

| Property | Unit | Value |
|---|---|---|
| Odour | | Strong |
| Density at 20°C | kg/L | 0.801 |
| Boiling range at 760 mm Hg | °C | 220 - 230 |
| Pour point | °C | < -30 |
| Vapour pressure at 20°C | kPa | < 0.012 |
| Flash point (PMC) | °C | 85 |
| Miscibility with water | mg/L | 172.5 |
| Purity | % m/m | 90 min. |
| Viscosity at 20°C | mm2/s | 45 |

Molecular Weight: 171,32 g/mol

Flash Point: 85 °C

Enthalpy of Vaporization: 46,12 kJ/mol

· Versatic acid: Versatic™ Acid 10, also known as neodecanoic acid is a synthetic, highly branched-C10 tertiary carboxylic acid made from mixing various carboxylic acids with the common formula $C_{10}H_{20}O_2$. These are:

- 2,2-Diethylhexanoic acid
- 2,2-Dimethyloctanoic acid
- 2,5-Dimethyl-2-ethylhexanoic acid
- 2,4-Dimethyl-2-isopropylpentanoic acid
- 2,2,3,5-Tetramethylhexanoic acid

Refering to its structure, this may be expressed as:

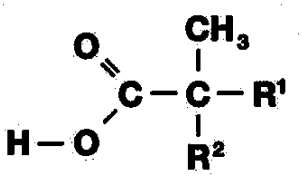


Fig 3: Versatic 10 molecule

where R1 and R2 are alkyl groups.

Table 7: Versatic acid 10 properties

| Property | Unit | Value |
|---|---|---|
| Odour | | Strong |
| Density at 20°C | kg/L | 0.91 |
| Boiling range at 760 mm Hg | °C | 270 - 280 |
| Pour point | °C | < -30 |
| Vapour pressure at 20°C | kPa | < 0.02 |
| Flash point (PMC) | °C | 129 |
| Miscibility with water | | Negligible |
| Purity | % m/m | 90 min. |
| Viscosity at 20°C | mm2/s | 45 |

As a synthetic acid, neodecanoic acid is typically first converted into an acid chloride or metal salt. This acid chloride is used in the production of peroxides for polymer production.

The manufacturer also suggests other common usages for the acid: Metal salts, e.g. Cobalt, Copper or Zinc salts of Versatic Acid 10, used in applications such as tire adhesives, paint driers, PVC heat stabilisers, chemical processing catalysts, unsaturated polyester cure catalysts, wood preservatives and fuel additives.

Also, and more importantly, the manufacturer highlights that Versatic Acid 10 acid is a very effective metal extraction agent that is particularly suitable for Nickel.

Table 8: Kerose properties

| Property | Unit | Value |
|---|---|---|
| Odour | | Strong |
| Density at 20°C | kg/L | 0.80 |
| Boiling range at 760 mm Hg | °C | 175 – 325 |
| Pour point | °C | < -30 |
| Vapour pressure at 20°C | kPa | 0,03 |
| Flash point (PMC) | °C | 38 |
| Miscibility with water | | Negligible |
| Purity | % m/m | 90 min. |

## 3.6. Atomic Emission Spectroscopy

After doing the experiments, the samples have to be analysed. Currently, there are various techniques which reveal, with more or less accuracy, the samples concentrations such as atomic emission spectroscopy (AES), inductive coupled plasma and so on.

Atomic emission spectroscopy is a technique capable of detecting and quantifying most of the existent elements. This technique analyses the colors of the light emited after exciting electrons within a sample. This makes that, by recognising the color of a flame (most of times a combined with colors from other species), the operator may be able to corroborate the presence of different species decomposing the beam of light into different frequencies.

These varieties of frequencies emerge from the emission of energy (in terms of light) by the excited electrons from the sample which are splitted by means of a prism. In fact, an important benefit of using emission spectrocopy is that the operating costs are usually lower, in comparison with other techniques.

However, even with its reliability, AES present a set of weaknesses. These come from the equipment quality such as how warm the flame can turn or how accurate is the method used to recognise the spectrum of light from the emited light.

Modern devices, such as ICP or MP AES are currently the most reliable equipments to ensure good results. In fact, the traditional AES devices can't stand a chance against MP-AES flame because is hotter and brighter (up to 6000ºC, 11000ºF) and also these are provided with high-accuracy detectors.


Fig 4: Atomic Emission Spectroscopy

The basic spectrophotometer's components are the torch, the sample, the monochometer, a detector and the measuring device.

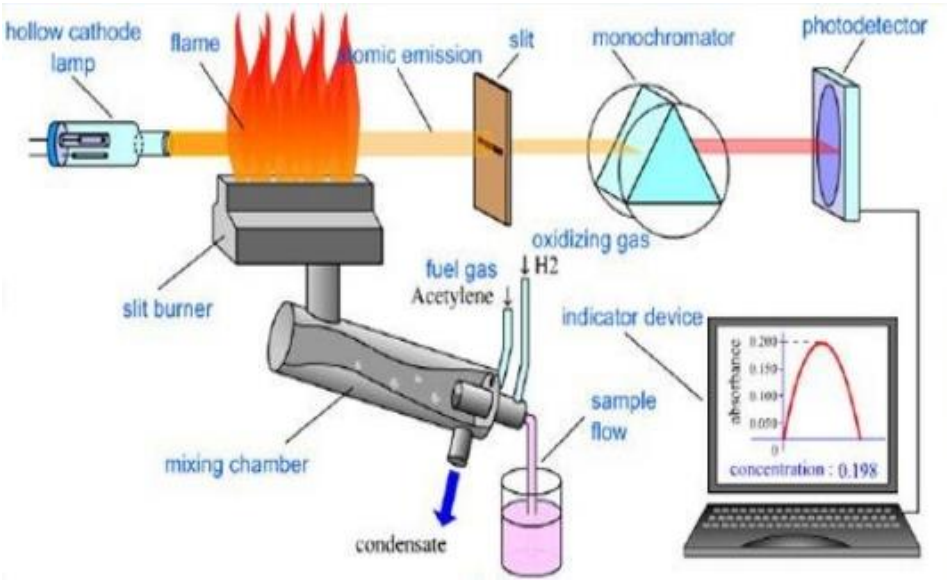


Fig 5: AES scheme

Once the sample has been atomized and excited by using the torch, that has to provide energy enough to produce the plasma, it emits a spectrum of light where, for every single metal, there is a particular spectrum of radiation that determines the presence of certain species.

This light is led to a detector, but previously, a monochrometer prevents scattered light to the detector, acting like a filter. Then a photodetector converts the light signal into an electric one and finally registered by a indicator device.

# 4. EXPERIMENTAL PART

## 4.2. Materials and method

### 4.2.1. Reagents

Main reagents:

- Bidistilled water. MW = 18,01 g/mol
- Cobalt standard for ICP. MW = unknown
- Cobalt sulphate heptahydrate. MW = 281,09 g/mol
- 1-decanol. MW = 158,28 g/mol
- Hydrochloric acid. MW = 58,44 g/mol
- Kerosene. MW = unknown
- Nickel standard for ICP. MW = unknown
- Nickel sulphate hexahydrate. MW = 262,15 g/mol
- PRIMENE 81-R. MW = 194,06 g/mol
- Sulphuric acid. MW = 98,08 g/mol
- Versatic acid 10. MW = 172,26 g/mol

Other reagents:

- Acetone. MW = 58,08 g/mol
- Alamine 336. MW = unknown
- Chinese extractant. MW = unknown
- Ethanol. MW = 46,07 g/mol
- Sodium bicarbonate. MW = 84,01 g/mol

### 4.2.2. Materials

- Becker. From 100 mL to 1000 mL
- Burette. Of 25 mL
- Flask cap.
- Disposable gloves. They can be made of latex or nitrile.
- Generic gripper.
- Glass flask.
- Pipette tip.

- Spatule.
- Support.
- Volumetric flask. From 5 mL to 1000 mL.

### 4.2.3. Instruments and measurement devices

- Magnetic agitator.
- Digital laboraty balance.


Fig 6: Balance COBOS "CB-Junior"

- Mechanic agitator.
- Microwave Plasma Atomic Emission Spectrometer.

Fig 7: MP-AES 4100

- pH-meter.

### 4.2.4. Method followed

The basic method used in each essay is the one that follows:

- First of all, it is prepared the set of aqueous solutions (stock solution) which is going to be the object of study. These include the 2 species to treat, cobalt and nickel.

  At the same time, the organic phases may be produced and, depending on the requirements or the nature of the experiment, some of them can be used in more than just a single experience or not. Following this criterion, more or less stock solution is made depending on the needings.
- Once prepared the aqueous and the organic solutions and set the funnels correctly, the extraction may begin by introducing a certain volume of aqueous phase and subsequently adding an amount of organic.

  Depending on the experiment, the amount of the phase will vary in order to achieve better results. However, the standard volume of aqueous and organic for each essay will be set as the same volume (5 mL) so the phase relationship hold is 1:1 (r=1).
- After filling the system with the liquids, a degree of turbulence is required to ensure a good contact between both phases. This is achieved by means of a mechanic agitator operating during 20 minutes at 140 RPM.

  Having reached a good contact, the glassware is placed firm and straight to the support structure where, due to gravity, both phases separate. This may take a few minutes or maybe several hours.
- Once both liquids are separated and they are clear (if not, or there is any anomaly it has to be written down), the phases are separated by turning the nut. The sample is collected in a test tube where the pH can be measured easily.
- Leaving in the funnel just the organic phase, the stripping takes place by adding a new aqueous phase high in protons. By doing this a new complex is generated and, at the same time, the protons are released. If the addition is good enough, almost all the metal will move to the aqueous phase. Having done several essays, to r=1 it is enough to introduce HCl 1M in order to achieve a good stripping.

  And following the previous steps, it is necessary to agitate the liquids during 20 minutes at 140 RPM and wait for their separation.
- To analyse the samples obtained and determine the extraction ratio of the experiments, it is used a MP-AES 4100 by Agilent Technologies.

  The analysis takes several operations which are:
  - Produce the dilutions of the samples to analyse.
  - Prepare the standards
  - Set the hardware
  - Run and configure de software
  - Do the analysis

### 4.2.5. Organic phase preparation

The organic phase is the one which contains part of the metal after the extraction. It is made from several compounds which, combined in different proportion, grant particular benefits.

The organic phase may be generated by 2 different ways:

- Outside the system: By mixing all the reagents inside a volumetric flask. This is especially interesting when it is produced a significant amount of stock solution or if the operatior has not skill enough to produce it inside the system.
- Inside the system: If it is not required such accuracy or if it is dealed with volumes big enough, the operation can be done inside the funnel introducing first the base (amine), then the acid and finally the kerosene.

All the amounts have to be calculated from density and purity data in order to have a close idea of the moles of each reagent within the system.

The initial organic phase will contain a 10% (v/v) of acid versatic 10, which is a common value to start the experiments due to its good results. Also, it will contain a part of PRIMENE 81-R that, due to its specs and stechiometry will be probably similar in terms of % (v/v). Moreover, kerosene will be added as diluent because of its good properties. A kind of modifier might be added to boost the process.

To start with, is not a bad measure to start with a stechiometric relationship between acid and amine.

Now, from the reagents specs:

Table 9: Organic reagents specs

| | Versatic acid 10 | PRIMENE 81-R | Kerosene | Decanol |
|---|---|---|---|---|
| MW (g/mol) | 172,26 | 194,06 | - | 158,28 |
| Density (g/mL) | 0,9 | 0,8056 | 0,78-0,81 | 0,8 |
| Purity (%) | 0,9 | >99,5% | purum | 99% |

To do the calculus, there are found 2 cases:

- A particular specification is within a defined range (e.g. density (0,8-0,85)). In this case, it will be used the average value.

- A particular spec. (purity) is found near to the 100% (e.g. purity>=99%). In this case, it will be used the minimum value.

Then, turning to the calculus:

- The molarity on versatic10 10% (v/v):

$$\frac{10mL\ v10}{100mL\ sol} * \frac{0.9\ g}{mL} * \frac{1000\ mL}{L} * \frac{1\ mol}{172.26\ g} * \frac{90}{100} = 0{,}47M\ versatic10 \quad (18)$$

$$\frac{0.47\ v10}{1L\ sol} * \frac{1\ mol\ 81R}{1\ mol\ v10} * \frac{194.062\ 81R}{1\ mol\ 81R} * \frac{1\ L}{1000mL} * \frac{1mL\ 81R}{0.8056\ 81R} * \frac{100}{100} * 100 \approx 11{,}3\% \left(\frac{v}{v}\right)\ 81R \quad (19)$$

However, before getting started, it is convenient to estimate the amount of organic needed to do an essay. By doing this, things like running out of organic in the middle of an essay, will not occur that easily.

To start with, it may be prepared 100mL so the maximum amount of funnels available is 20 (19). That is to say that it is posible to do, for instance, 3 experiments with 6 funnels. This amount is produced in base to the requirements and the hardware available so it can be modified but the important part here is to use always the same solution within a single experiment so the error related with the organic preparation is minimized.

For the case of 100mL:

$$100mL\ sol * \frac{10mL\ v10}{100mL\ sol} * \frac{0.9\ v10}{1mL\ v10} = 9g\ v10 \quad (20)$$

$$100mL\ sol * \frac{11{,}3mL\ 81R}{100mL\ sol} * \frac{0.8056\ 81R}{1mL\ 81R} = 9{,}1g\ 81R \quad (21)$$

$$100mL\ sol * \frac{5mL\ deca}{100mL\ sol} * \frac{0.8\ v10}{1mL\ deca} = 4g\ deca \quad (22)$$

Sometimes to make faster the phases separation, it is convenient to add another specie that does the trick. These are called “phase modifiers”.

When the operator has enough skill, there is no need to do it by checking the weight, just setting correctly a pipette and finally, fullfilling the flask up to the mark with diluent. It must be stired properly in order to mix all the compounds due to their density difference.

### 4.2.6. Aqueous phase preparation

For the aqueous phase the operation is even easier due to there is only one way to produce it. The method is as simple as calculate the molarities of nickel, cobalt and sulphate desired, then it is just to transform this requirements to the mass necessary for each solution.

$$molarity\ Me = ppm\ Me * \frac{1\ {}^{mg}/_{L}}{1\ ppm} * \frac{1g}{1000\ mg} * \frac{1\ mol}{MW\ g\ Me}$$

Using the same pattern for both metals:

$$molarity\ Ni\ (M) = ppm\ Ni * \frac{1\ {}^{mg}/_{L}}{1\ ppm} * \frac{1g}{1000\ mg} * \frac{1\ mol}{58{,}71\ g\ Ni}$$

$$molarity\ Co\ (M) = ppm\ Me * \frac{1\ {}^{mg}/_{L}}{1\ ppm} * \frac{1g}{1000\ mg} * \frac{1\ mol}{58{,}43\ g\ Co}$$

And for the sodium sulphate:

$$molarity\ of\ sulphate\ (M) = mols\ of\ nickel - mols\ of\ cobalt$$

And the mass necessary for 100 mL of cobalt/nickel (500/5000) ppm with 0.5M of sulphate:

$$mass\ \ NiSO_4 * 6H_2O\ (g) = mols\ Ni * MW_{NiSO_4*6H_2O} * \frac{100\ mL}{1000\ mL}$$

$$mass\ CoSO_4 * 7H_2O\ (g) = mols\ Co * MW_{CoSO_4*7H_2O} * \frac{100\ mL}{1000\ mL}$$

$$mass\ Na_2SO_4 * H_2O\ (g) = mols\ SO_4 * MW_{Na_2SO_4*H_2O} * \frac{100\ mL}{1000\ mL}$$

- Above, mass (metal) means the mass of salt added.

Having calculated the amounts of salt, it is just weight it with the balance and add bidistillated water to fulfill the desired volume. Also, it is quite common to apply some agitation and some heat because the salt of sodium is especially difficult to dissolve.

### 4.2.7. Standards preparation

In order to generate a good calibration line, it is essential to prepare correctly a sequence of standards. These are compared by the MP-AES with the samples and once the lecture is done, the results are obtained.

The standard samples used go from 0 ppm, with no solute, to 10 ppm and are obtained from a stock solution of nitric acid 0,5% (v/v) with a small amount of sodium sulphate that makes a concentration of 0,001M of sulphate.

From this stock solution, a second solution which contains the standard is generated. This is achieved by means of adding 1 mL of cobalt and nickel standard in a volumetric flask and reach the volume of 100 mL adding stock solution.

The next part is just defining the ppm of the standards, for example:

- 0, 2,5, 5, 7,5 and 10 ppm of metal (Ni/Co).

This range of concentrations is chosen due to how much diluted the samples are so, expecting to have 5000 ppm and 500 ppm in the stock solution, the dilutions will be 50 to measure cobalt and 500 to measure nickel.

## 4.3. Previous action

To achieve the main target of this project, which is to separate nickel and cobalt with an specific extractant, several experiments have been done previously, starting with choosing a good extractant. This part is extremely important because there are extractants that do not extract any metal or almost nothing.

Starting from the idea that the extractant synthesized has to be neutral to ensure its correct behavior in a continuous process, the research could start by selecting several non-water miscible organic acids and several amines (primary, secondary and tertiary).

Following the advice of the experts, the experiments should move into the right direction. However, the kind and concentration of solute is also an important factor so all these clues should be enough to create a starting list of possible candidates.

In the workshop there is a wide variety of amines but, the starting essays have been done with Alamine 336, PRIMENE 81-R and a chinese extractant badly labelled.

After several essays with Alamine 336, Chinese extractant, oleic acid and DEHPA, the extraction rates are really bad.

However, the usage of PRIMENE 81-R involves an extraction rate enough to corroborate that its choice would give an interesting opportunity to study how good is its behavior in the current conditions.

In the table below are shown the decisions made based on the performances obtained.

Table 10: Discarding and accepting amines to study

| | Approximate performance | Suitable of studying |
|---|---|---|
| PRIMENE 81-R + v10 | > 50 % | YES |
| Chinese extractant + v10 | ≈ 0 % | NO |
| Alamine 336 + v10 | ≈ 0 % | NO |

As shown above, it is not interesting to invest time doing more essays with Alamine336 or the Chinese extractant. Therefore, the reagent used is PRIMENE 81-R which shows higher extraction ratios and separate cobalt from nickel:

Table 11: First essay with 81R+v10

| | (mg/L) Co | (mg/L) Ni | Co performance (%) | Ni performance (%) |
|---|---|---|---|---|
| initial1 | 531,63 | 488,39 | | |
| 5% volamin. | 371,23 | 470,12 | 30,17 | 3,74 |
| 10% volamin. | 202,45 | 454,23 | 61,92 | 6,99 |
| 15% volamin. | 101,11 | 445,09 | 80,98 | 8,87 |

In the previous table, the experiments have been done with an initial concentration of 500 ppm of Ni and 500 ppm of Co because, at these stage, the problem solution was not defined, however, its success may be extrapolated. Alamine 336 and the Chinese barely give a 10% of extraction without favouring a concrete metal (there's no separation). The results may be checked in the Excel document "Exp.Mod.xlsm" EXP.0.

### 4.3.1. First approach to v10/81R

As mentioned before, the extractant used is a combination of versatic acid 10 + PRIMENE 81-R which will be called in this project as "v10/81R". According to literature, the PRIMENE 81-R and other similar products, e.g. JMT, respond correctly to extraction processes. In the current experience it is going to check how behaves the extractant without adding extra sulphate.

Table 12: PRIMENE series products

| Product | Composition |
|---|---|
| PRIMENE JMT amine | Mixture of highly-branched C16 to C22 tertiary alkyl primary amine isomers |
| PRIMENE81-R amine | Mixture of highly-branched C12 to C14 tertiary alkyl primary amine isomers |
| PRIMENE RB-3 amine | Mixed tertiary alkyl primary amines |
| PRIMENE MD amine | Menthane diamine |
| PRIMENE TOA amine | t-Octylamine |

However, due to the the amount required of nickel and cobalt provided by sulphate salts, the results are close to a extraction at 0,1 M. Below are plotted the results for this first approach.

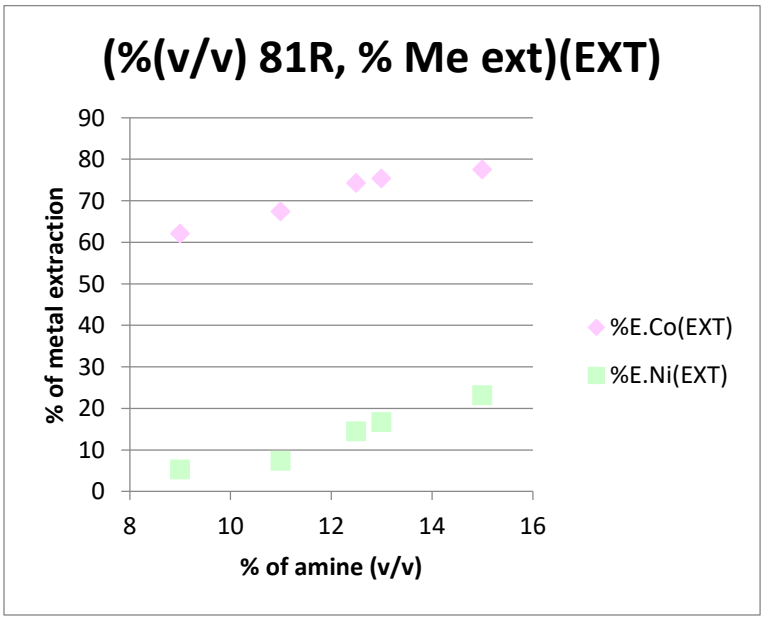


Fig 8: Changing %(v/v) of amine - (%volamine,%Me.Extracted)

It seems that by increasing the proportion of amine involves a higher extraction ratio. However the behavior is not linear so it may represent an interesting subject of study and also an interesting chance to use β and look how it responds and its magnitude.

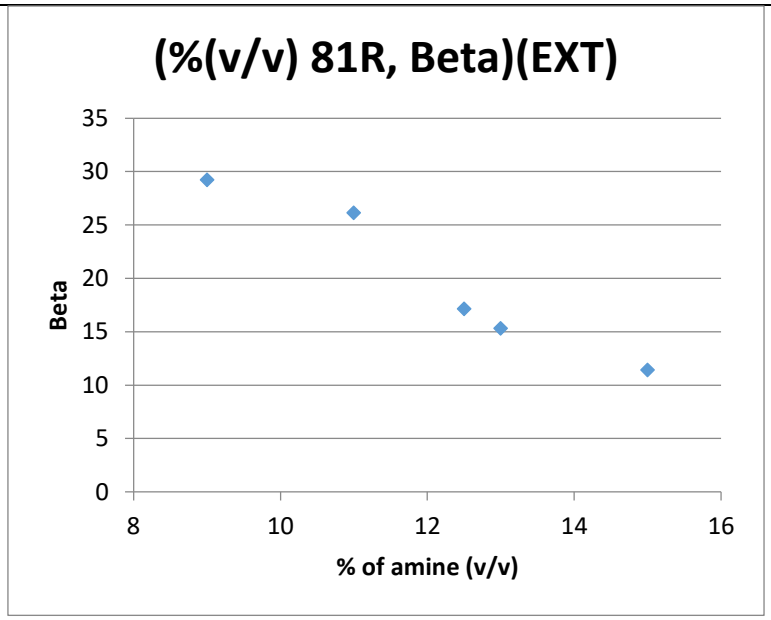


Fig 9: Changing %vol of amine - (Beta,%Me.Extracted)

Following the hypothesis proposed, it appears to be that unlike the extraction the maximum separation is achieved in 9% of 81-R. Looking closely the trends of above it can be identified that the extraction stabilizes after the 12,5% (v/v) so increase the amount of amine much more has no point. Instead, following the tendency of the % of metal extracted it may be seen that reducing the proportion of amine (<9%) could give even greater results even though the nickel starts to stabilize as well.

## 4.4. Experiments design

Normally, to do these sort of studies, there is a sequence of experiments that follow a particular order. From the results of the first experiments the following ones take a shape so in a certain way, the last ones depend on the first ones.

Here it is followed the same praxis, so the experiments are in concordance with the first experience which is determine the propoertion of PRIMENE 81-R and versatic acid 10.

However, several changes may be done conveniently when required, always aiming to separate the metals

Having done this, the order of the experiments may vary if the same proportion of extractant is conserved. However, the study of sulphates is a good way to continue because it is a good way to see how this extractant respond with variating a diferent variable not related with the organic phase constitution.

From this point, the countercurrent process can be done and after, the remaining experiments to fulfill the data required. This set of data will permit to evaluate even more the extractant generated and, from this point, create a mathematic model.

The data necessary to construct the model are taken from the extraction of the metals individually, because a “mixed model” would be very hard to pose.

## 4.5. Study of the extraction fixing the volume of v10 and variating the amine

In the current study it is aimed to know the concentration of extractant which enhances the metal separation the most. Therefore, it has been decided to fix the amine (v10) and the decanol (if there is any) whist the other (81R) varies.

The scan of measurement starts from the 11% of amine and, by raising and lowering the percentage, a trend which shows the extraction ratio may be generated.

In these essays, as commented previously, it will be used an r=1 and just 5 mL of each phase due to the essay characteristics.

The register of all the calculus may be found in the annex. Below there is the general expression to prepare the organic considering an equimolar relationship between v10 and 81R:

$$mass\ of\ extractant = \frac{MW_{81-R}}{purity_{81-R}} * \frac{purity_{v10} * volume_{v10}}{MW_{v10}}$$

After following the method mentioned before and measuring, a particular trend for cobalt and nickel is obtained. Below it is shown the trend plotted in a diagram (Available in Exp.Mod.xlsm (EXP.1)):

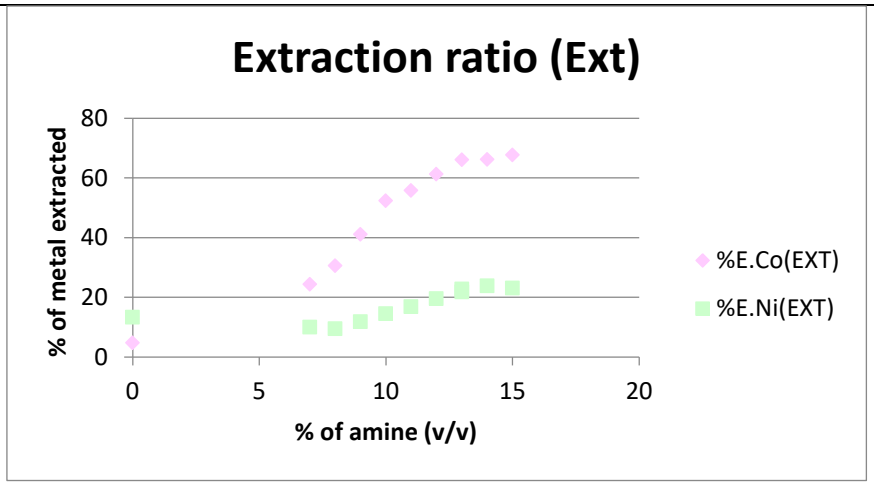


Fig 10: EXP.1 (%volume of amine, %Extraction)

In the previous graph (note that pink: goes for cobalt and green for nickel) it can be seen that there is a slight difference between this results and those obtained in point 0. The differences due to the presence of sulphates will be discussed later but at first sight it can be seen that the increase of this certain kind of salt reduces the extraction performance.

Turning back to the extraction ratio, it can be seen that it stabilices in the values over the 13 %(v/v) of PRIMENE 81-R, reaching its maximum performance around the 13%.

On the other hand, the extraction performance is not the variable to maximize but the separation. In the graph below it is represented the several values obtained for the β which stablish the best operating range.

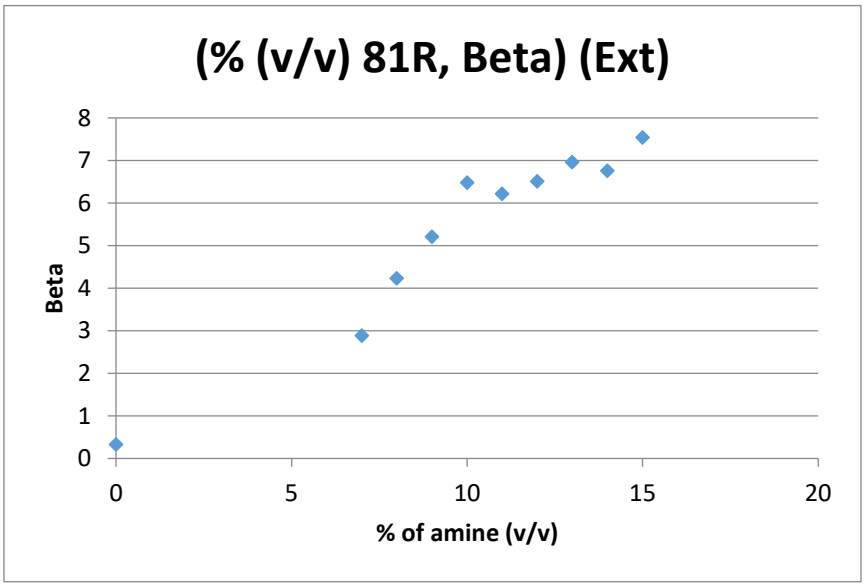


Fig 11: EXP.1 (%volume of amine, Beta)

It seems in the 15% tends to go even higher, however the concentration chosen is 11% because it is a point good enough where the β stabilizes and at the same time is the mathematical equimolar point.

From now on, the proportion of v10 and 81R is fixed according to this value.

## 4.6. pH Measurement

As mentioned in "The aqueous phase" 3.3.4.1, it is very important to check the evolution of the pH related to the extraction process in order to see if $H^+$ are generated. To avoid undesired effects such as the process stopped due to the saturation of protons, it is vital to make sure that the hypothesis of a neutral extractant is true.

In the following chapter is is going to see if data support this hypothesis or not.

Below is shown the set of thata that comes from the "amine variation" EXP.2, "Extractant dilution" EXP.3 and the "isotherm construction" EXP.5.

Table 13: Amine variation pHs

| %(v/v) 81R | Ni/Co pH after Ext |
|---|---|
| 7% | 6,21 |
| 8% | 6,52 |
| 9% | 6,76 |
| 10% | 6,91 |
| 11,3% | 7,13 |
| 12% | 7,22 |
| 13% | 7,39 |
| 14% | 7,41 |
| 15% | 7,52 |

In the previous table it is seen that the pH increases as the %(v/v) of amine rises. Being 6,5 the pH of the initial, it appears to be that the most neutral extractant is achieved in the 8%. Above this point, there is an excess of amine so there is a pH > 6,5.

Table 14: Extractant dilution pHs

| %(v/v) v10 | Ni/Co pH after Ext | Co pH after Ext | Ni pH after Ext |
|---|---|---|---|
| 2% | 6,71 | 6,8 | 6,71 |
| 4% | 6,75 | 7,75 | 7,15 |
| 6% | 6,79 | 7,75 | 7,13 |
| 8% | 6,93 | 7,78 | 7,18 |
| 10% | 6,96 | 7,79 | 7,15 |
| 13% | 7,05 | 7,81 | 7,17 |
| 16% | 7,07 | 7,82 | 7,18 |
| 20% | 7,13 | 7,84 | 7,22 |

In this table the trend is pretty similar but the pH are slightly higher due to the chosen extractant (10/11,3).

Table 15: Sulphate variation pHs

| MOLARITY | pH (before) | pH (after) |
|---|---|---|
| 1,00 | 6,96 | 7,08 |
| 0,75 | 6,52 | 7,07 |
| 0,50 | 6,50 | 7,07 |
| 0,40 | 6,40 | 7,05 |
| 0,25 | 6,20 | 7,04 |
| 0,10 | 5,97 | 7,03 |

Here it may be seen that the common point still gives the same result, as expected and, as increases the sulphate molarity, the pH after extraction does it too.

Table 16: Isotherm pHs

| ppm of Co | Initial pH | pH after Ext |
|---|---|---|
| 100 | 6,44 | 7,09 |
| 200 | 6,47 | 7,11 |
| 300 | 6,49 | 7,15 |
| 400 | 6,51 | 7,15 |
| 500 | 6,53 | 7,17 |
| 800 | 6,58 | 7,18 |
| 1000 | 6,59 | 7,20 |
| 2000 | 6,6 | 7,27 |

In this table it is seen that the trend responds to the 2 last statements, one referring to the amine excess and the extra sulphate (this coming from a different source).

As expected, working slightly over the neutral point, the pH does not decrease. It is very convenient to prevent the system from delaying.

## 4.7. Study of the extractant variation by adding more diluent

### 4.7.1. For a mixture of metals Ni/Co 5000/500

This part focuses on the necessary amount of extractant to do the job. Basically it is just preparing a concentrated mixture of extractant, following the proportion decided in the previous point "Organic phase" 4.2.5 which is diluted in kerosene to obtain a set of concentrations of this extractant.

Starting from a concentrated mixture of extractant which contains a 22,6% of 81R and a 20% of v10 it is interesting to produce a second stock solution from this one (11,3%/10%) because there are a whole bunch of essays that require a low volume of the concentrated mixture. Therefore, using this second solution as a wildcard, the probability of committing errors during the organic phases preparation decreases. Then, by adding kerosene in different proportions, the whole range of concentrations is achieved.

Doing a scan of values from 2% to 20% appears a trend that suggests an important increase throughout the addition of more extractant the extraction ratio starts to stabilize. In the following graph are plotted the results.

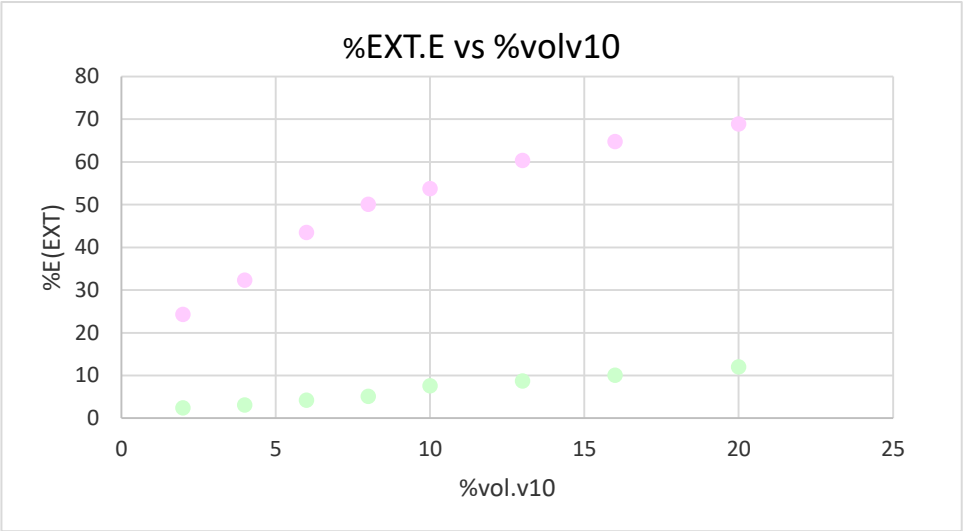


Fig 12: EXP.2 (%volume of amine, %Extraction)

However, to evaluate correctly the results it is convenient to use the β so the point or range of values that correspond to the optimal extraction may be found. Below is shown the graph with the β for this experiment. *Notice that in the X axis the variable is now the % in volume of v10 instead of 81R.

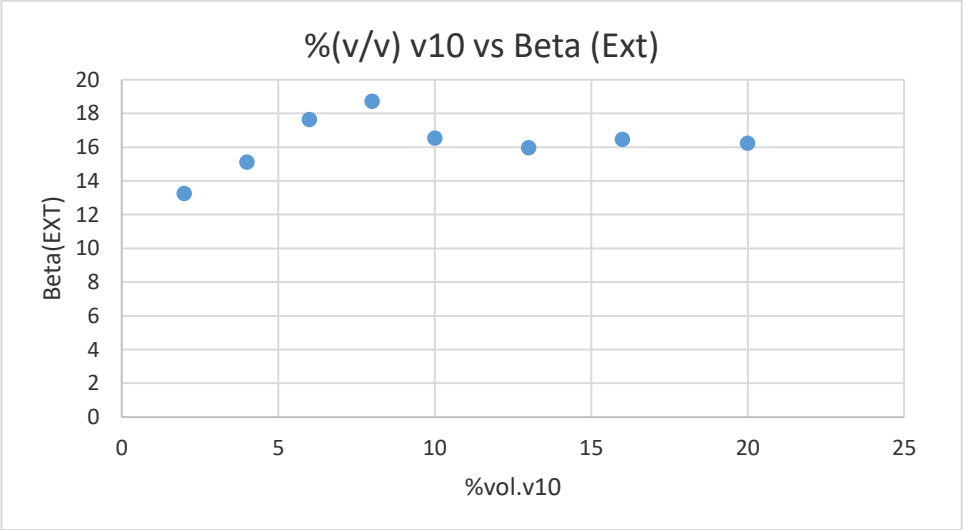


Fig 13: EXP.2 (%volume of amine, Beta)

As the graph suggests, the maximum separation is achieved around the 8 % but the value taken to do the next experiments is the one which corresponds to the 10% because it also achieves a good separation and there are data of this proportion from previous essays that can be compared with.

In other circumstances, the decision would be choosing the optimum value but to do the next experiments the current choice hold its own very well.

### 4.7.2. For the metals individually

For the metals individually, the extraction percentage may be also checked by using the same method. This, nevertheless, is using an aqueous phase that is containing just one metal and the additional salt of sodium that supplies the sulphate to reach 0,5M of sulphate.

This essay is particularly interesting to see how the solute presence makes the extraction vary. In this case, the comparison is made with cobalt 500 ppm and nickel 5000 ppm which, due to the high concentration of cobalt, it might give place to bizarre lectures while the measuring part but as an example fits well and also permits to reuse data.

The graph below shows the results of extraction form metals individually in the same way as 4.7.1:

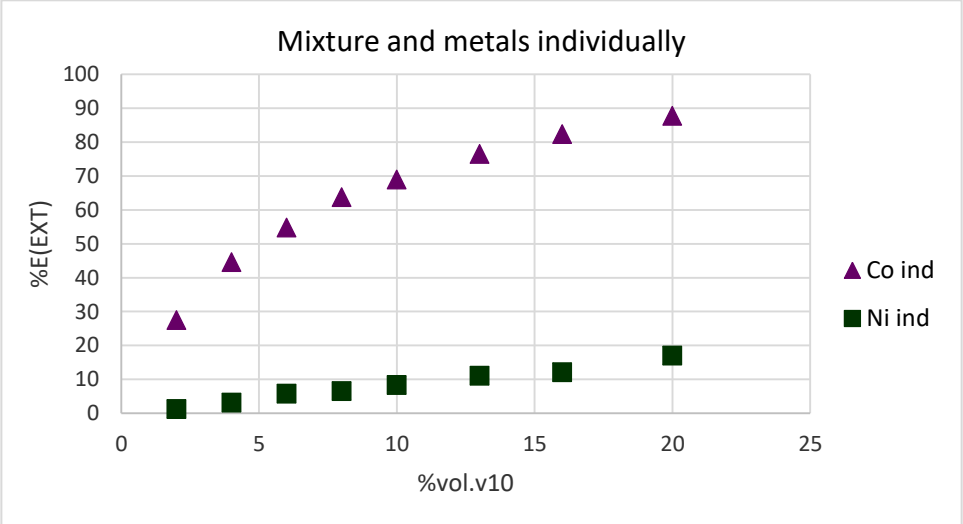


Fig 14: EXP.1 (%volume of amine, %Extraction) for metals individually

At first sight, the trends may look the same as 4.7.1, however there are slight differences. However, it seems that it starts to stabilize once passed the 15% of v10 (v/v).

In the next section (4.7.3) is seen more in detail the various aspects that change by separing separately or altogether.

### 4.7.3. Comparison between metals mixed and individually

This section contrasts both experiences, mixed and individual metal solutions which may be useful to quantify how a solute interferes during the extraction of the other.

The graph below gives a view of how the percentages are affected:

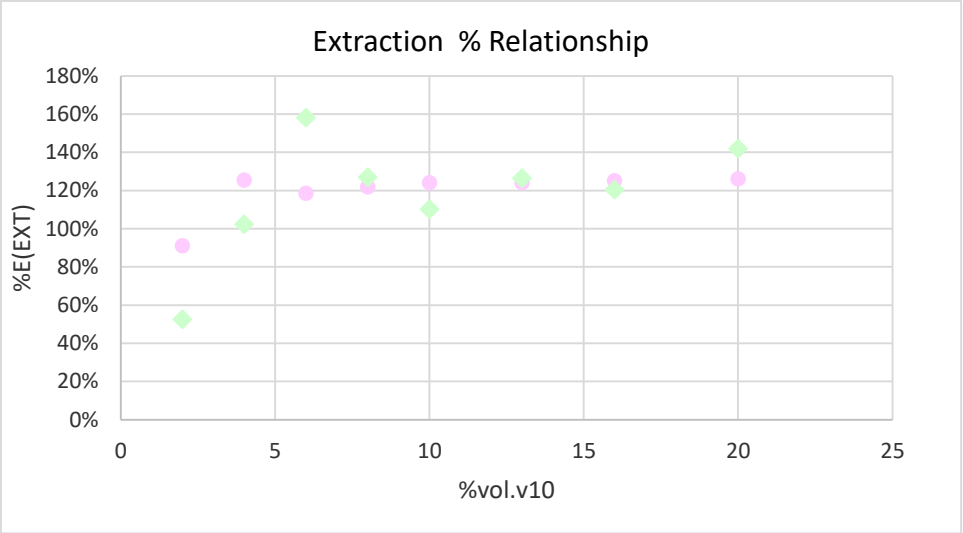


Fig 15: Difference between mixed and individual metals

As seen, it could be ensured that the metals individually provide in general better results than the mixture. However, from 0 to 4% of v10 (v/v), it seem that it cannot be ensured being the extraction notoriously worse, especially for nickel.

For the range chosen to do the essays, the values are pretty stable so it is assumed that for each metal individually its performance increases a 20%.

The following graph plots the extraction percentages, showing how they evolve as the % of extractant increases.

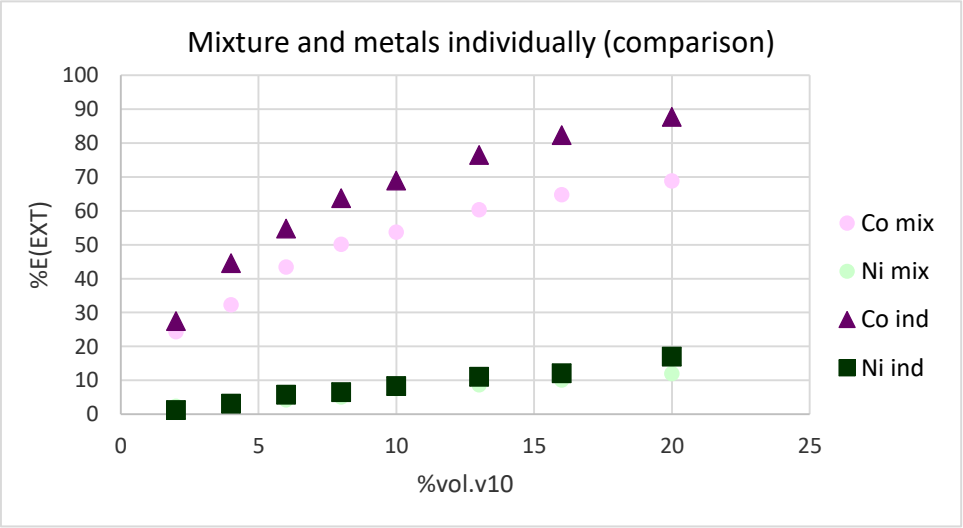


Fig 16: Comparison: All data put together

It might be understood that cobalt suffers more change than cobalt but, having a look to the previous graph it is just that cobalt experiences a higher overall extraction because both proportions related to the metals individually and mixed save a similar proportion.

## 4.8. Study of the variation of sulphates

In the current study is made a sulphate variation of the aqueous phase. Then, being fixed the organic phase as 10% of versatic 10 and 11,3% of PRIMENE 81-R an scan of sulphate values is done fixing also the amount of metal at 5000ppm of nickel and 500ppm of cobalt. The range studied goes from 0,1M to 1M.

From previous experiences, it is known that sulphate may generate certain impact during the extraction. Now it is going to be quantified by means of the extraction within various funnels to generate a tendency. According to the generic reaction below, sulphates are found in the extraction process in both phases, just as happens with the metal. From below, it can be understood that sulphates and metals are saving a certain relationship given by the constant $K_{ext}$.

$$Me^{2+} + SO_4^{2-} + 2\overline{RH_2NHA} \leftrightarrow MeA_2 + \overline{(RH_2NH)_2SO_4} \quad (23)$$

At the same time, some other species may appear. These follow a particular stoichiometry and have a K of formation involved. However, its formation generally affects in a bad way on the extraction due to the metal taken by the complexes will not have the chance to join the extractant. The following stoichiometries are the most likely to be found in the process.

$$Ni^{2+} + SO_4^{2-} \leftrightarrow NiSO_4 \quad ; \quad \delta 1_{Ni} = 194{,}98 \quad (24)$$

$$Ni^{2+} + 2SO_4^{2-} \leftrightarrow Ni(SO_4)_2^{2-} \quad ; \quad \delta 2_{Ni} = 10{,}47 \quad (25)$$

$$Co^{2+} + SO_4^{2-} \leftrightarrow CoSO_4 \quad ; \quad \delta 1_{Co} = 218{,}78 \quad (26)$$

Where δ is a coefficient of formation of the compounds formed by the metals + sulphate. The values are extracted from MEDUSA.

The method follows the same pattern as the previous experiments so the phase relationship is 1:1 in extraction and stripping so there is not any difficulty. However, here there are required several aqueous phases which can be made from 2 stock solutions mixed in different proportion or one by one. Depending on the number of essays it would be more convenient one or the other. The current choice has been to produce them one by one controlling the amounts of salt precisely.

On the other hand, because of the salts chosen provide some sulphate, the calculus are made according to this fact. That is why the first point (0.1) has to be made with extreme care because it

barely contains additional salt. However, it does not represent any troble when the amount is big enough or the first point to consider has some distance to the "zero". The spectrum chosen to do the study is (0,10, 0,25, 0,40, 0,50, 0,75, 1,00M).

Before the results discussion, it is interesting to comment that as the concentration of salt increases, the blue color after the extraction turns slightly less blue so it gives some clues about the extraction decreases. Just the opposite happens with the facility to turn the phases transparent and clear after stripping, more concentration makes it slower.

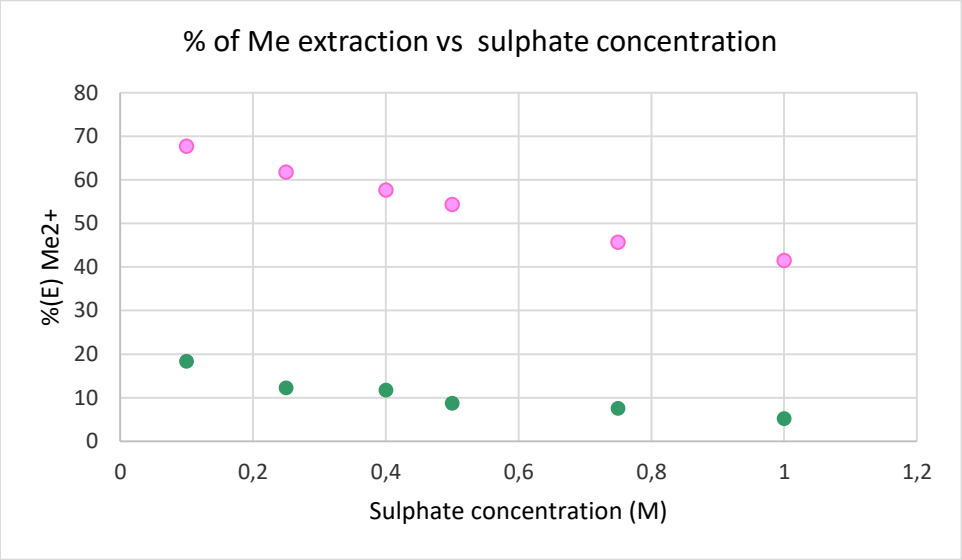


Fig 17: Sulphate variation vs % of metal extracted

In the graph above it may be observed how decreases the extraction as the sulphate concentration increases.

On the other hand, the 0,1M increases the overall extraction having almost a 70% of the cobalt extracted aigainst

## 4.9. Study of the decanol variation

In this part it is going to be discussed the influence of adding decanol to the organic phase. This decanol might reduce the time spent in each stage when the phases separe which is especially interesting when the system stabilization is reached after a lot of stages. However it is convenient to determine a % of volume enough that does this task but at the same time it does not affect the % of extraction that much.

To evaluate this behaviour it has been done an experiment with 1-decanol at different concentrations so a trend may be generated.

The current conditions are a phase relation 2:1 plus an additional funnel 1:1 to evaluate that the aqueous phase correspond to the used in previous essays.

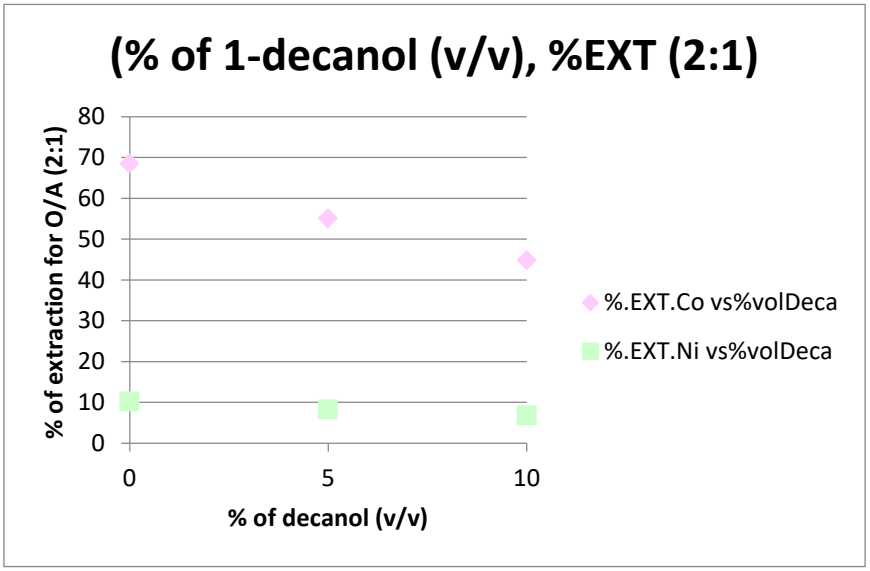


Fig 18: %(v/v) of 1-decamol vs %Ext (r=2)

In the graph above it may be seen that the trend tends to reduce the metal extracted as the amount of decanol increases. At first sight it could be seen as a drawback because it affects the overall performance of the operation. However the time of phases separation reduces sharply, from 20-30 minutes to 5 minutes in the extraction and in the stripping is even more remarkable where the aqueous phase clarifies in a few minutes instead of several hours.

Moreover, it is convenient to think about how much cobalt remains into the aqueous phase, which is the target medium and the metal separation, our main goal.

There is an important consideration also related with the organic transport. After several hours, the phases coloration changes slightly but after some days, the organic phases which still contain metals becomes green when initially was dark blue. This may be caused due to some kind of oxidation reaction.

As a conclusion, it would be interesting to claim the possibility of 1-decanol usage, but just an amount enough to make easier the separation without putting into risk the separation. For instance, choosing a 5% of decanol, the results show that the separation achieved is preety similar to 0% of decanol in a phase relation 1:1. This is an important consideration to evaluate the results. Additionally, it is obtained a lower time of separation so, in other circunstances where the economic factor was not that important, it might be considered as a possible and feasible measure.

To see the results in more detail, please address to Exp.Mod.xlsm (EXP.8).

## 4.10. Study of the phase relationship variation

In the current study is being checked how affects the variation of r by varying the organic phase and preserving a fixed extractant 10%/11,3% of (v10/81-R). This makes that the overall volume of the system change but, moreover, it is going see if this change also affect by a different way.

Theoretically, each funnel would contain the same amount of extractant that the study 4.7.1 so the resultsapparently should not differ too much. However, there are more factors that could change in minor or major degree the results of both experiences.

Below it is shown both results in the same graph, giving a view of how distinguish one from other:

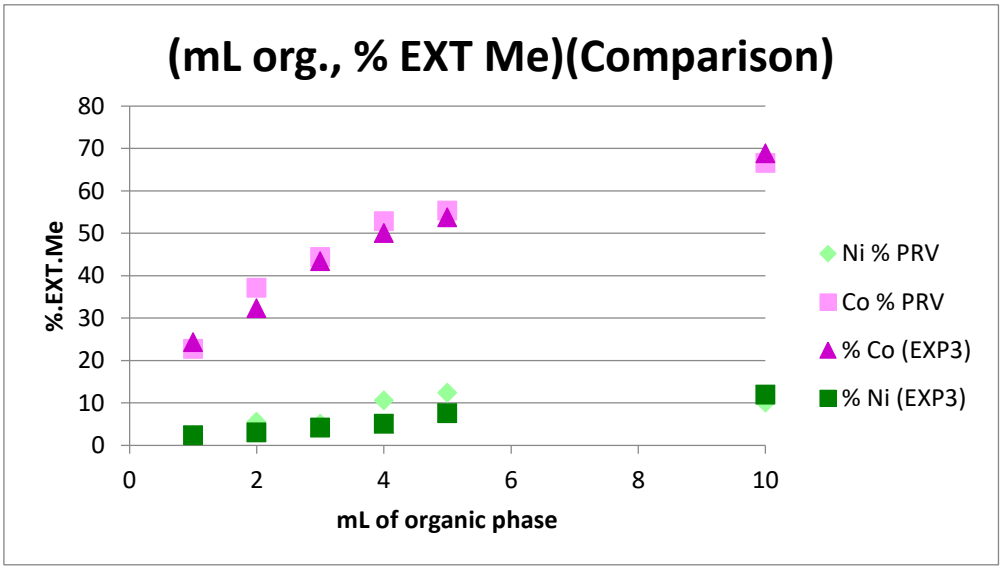


Fig 19: mL of organic vs % of metal extracted

Having just a quick view on the graph, it might be concluded that, underestimating the possible experimental error, both tendencies show the same results so it is pointless to go beyond.

However, it might be said that the 1-decanol containing gives a little more extraction, probably due to better contact between phases (lower viscosity). They both have followed the hypothesis of t = 20 min.

To see the results in more detail, please, address to Exp.Mod.xlsm (Exp.9).

## 4.11. Extraction isotherm

In this chapter it is aimed to determine the cobalt isotherm for a liquid-liquid extraction using a solution 10% of v10 and 11,3% of 81R and a liquid solution with a sulphate concentration of 0.5M experimentally.

It is only made for cobalt because nickel may be considered as constant, for the current process. Cobalt here is the key component.

It is understood by isotherm as the relationship between a particular solute diluted into both phases in equilibrium. It gives information about the maximum amount retained during an extraction with a particular extractant in a certain set of conditions (pH, temperature, concentration, sulphate presence).

The isotherm is obtained from the concentration of the overall metal transferred to the organic phase against the remaining metal in the aqueous.

This set of data permits to calculate the curve used to know the stages needed by McCabe-Thiele.

The main target here though is to determine the theoretical number of stages for a countercurrent continuous process, in first place, and, secondly, do the model so this one will permit to compare the theoretical data with the experimental.

The method here starts from the general method, which consists on preparing several funnels (r=1) doing an extraction with the same product and the same concentration (organic) but varying the metal cargo and fixing the salt concentration (aqueous). The essays include only the mixture of cobalt/nickel being the variable the cobalt concentration because, from previous experiments it has been seen that cobalt is the one which really “moves” from one part to another.

In order to produce a curve good enough, it is necessary to establish a set of values to do the scan. These may be, 100, 200, 300, 400, 500, 800, 1000 and 2000 ppm for cobalt and 5000 ppm for nickel and are produced from 2 stock solutions, one concentrated in cobalt and other cobalt-free.

The strippings are done with HCl 1M.

RESULTS

At first sight, it is pretty clear that as the concentration of cobalt increases the color of the initial solution changes. This occurs especially in concentrations over 500 ppm where it turns a kind of green/brown tone. Their differences are even more notorious once the extraction is complete, having a sequence of blue tones, slightly blue for 100 ppm and a deep dark blue for 2000 ppm.

In the following graph is shown the experimental isotherm obtained from the cobalt variation:

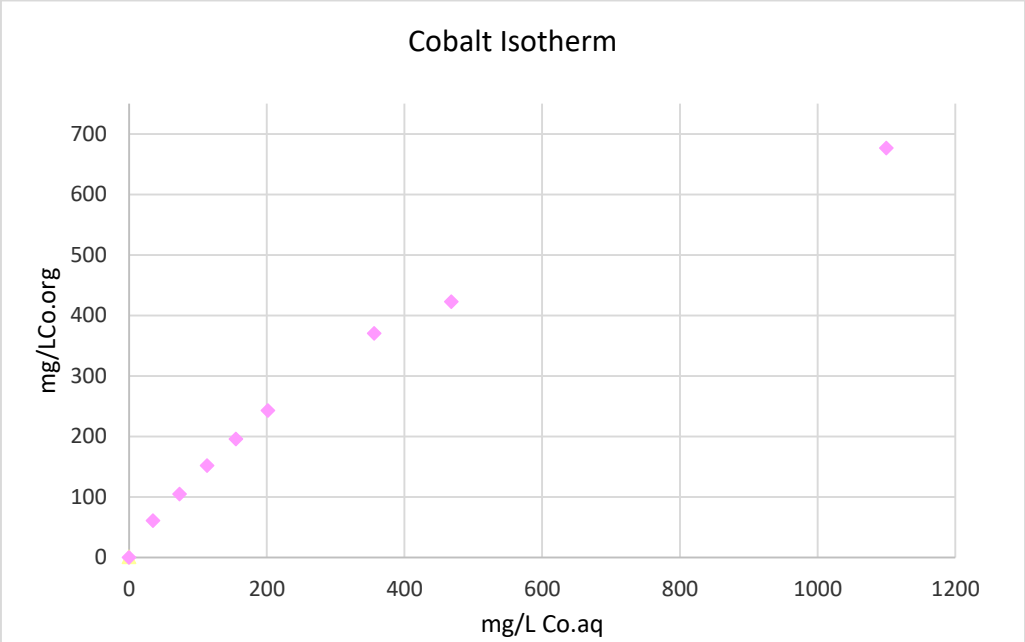


Fig 20: Cobalt isotherm (0-2000 ppm of Co)

Due to the concentration selected, it is more convenient to take a zoomed vision of the graph above.

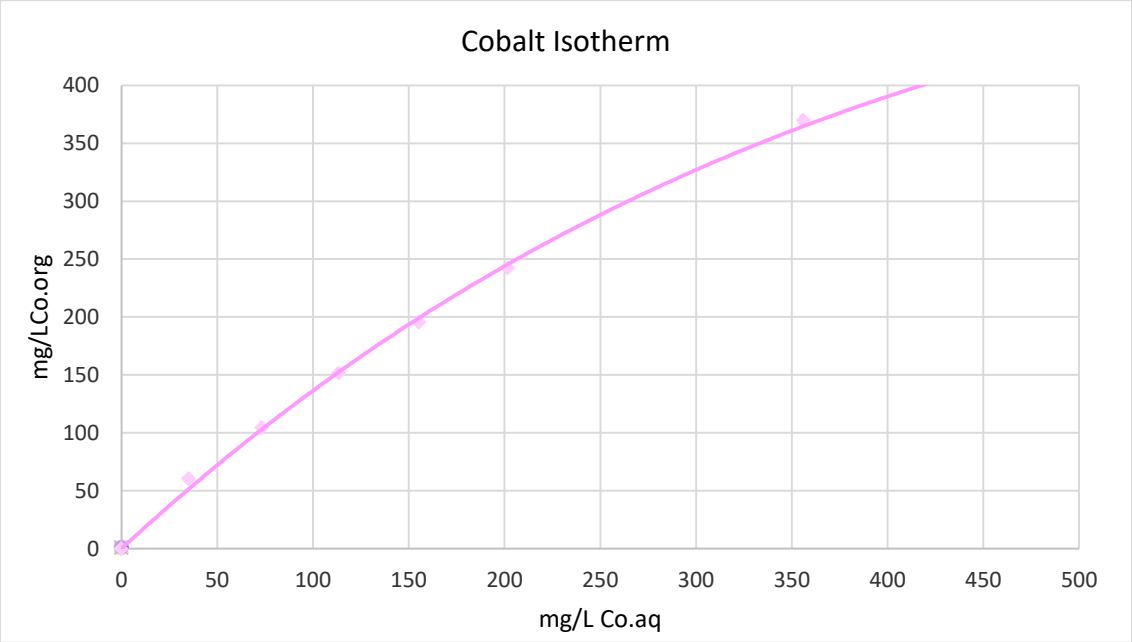


Fig 21: Cobalt isotherm + tendency curve

Having these results plotted it can be added a trend curve which helps to construct the McCabe-Thiele graph more easily and then, it is adjusted in order to obtain the theoretical number of stages.

To see the results in more detail, please, address to Exp.Mod.xlsm (Exp.5).

## 4.12. Simulation of a countercurrent extraction process

In this chapter, it is aimed to determine whether the nickel/cobalt separation of an aqueous solution by means of a multistage process may be carried out experimentally. The data obtained will be compared after with the model obtained in chapter 5.

To determine the theoretical stage number is used the McCabe-Thiele method which gives an intuitive view of the mass balances and the equilibria for a metal in certain conditions.

From previous experiments it has been checked that the metal which has a higher extractive ratio is cobalt. However, it is severely affected by the presence of nickel in mixture, as seen in 4.7.3. This might be the result of having such a concentration of nickel.

However, the data of the isotherm may be used to do the countercurrent simulation and following the relation below it can be obtained the number of stages.

$$w_{aq} * x_{n-1} + w_{org} * y_{n-1} = w_{aq} * x_n + w_{org} * y_n \quad (27)$$

And ordering the different terms:

$$y_n = \frac{w_{aq}}{w_{org}} * (x_{n-1} - x_n) + y_{n-1} \quad (28)$$

These relationships from above come from a mass balance applied to a stage n, for instance. This stage will gather a particular number of mass flows with concentrations associated and it is typically represented as:

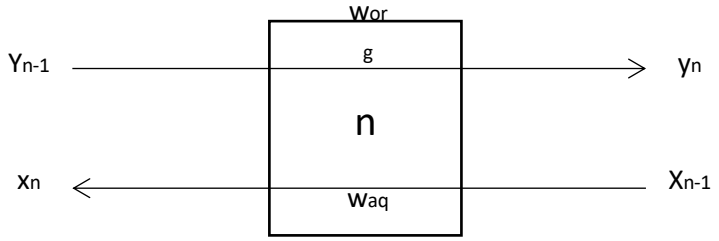


Fig 22: Stage scheme

From the slope of the line, which corresponds to the phase relationship (r), it may be generated the operating line so any modification on the phase relationship is changing the line slope.

Now, stablishing a phase relationship enough to avoid infinite stages McCabe-Thiele can be applied. As seen below, with r=1 the experience is not feasible, decreasing the phase relationship to 0,5, the number stages required to achieve a very good separation <10ppm of cobalt at the end of the process is just 4, and it may be emulated by the usage of funnels.

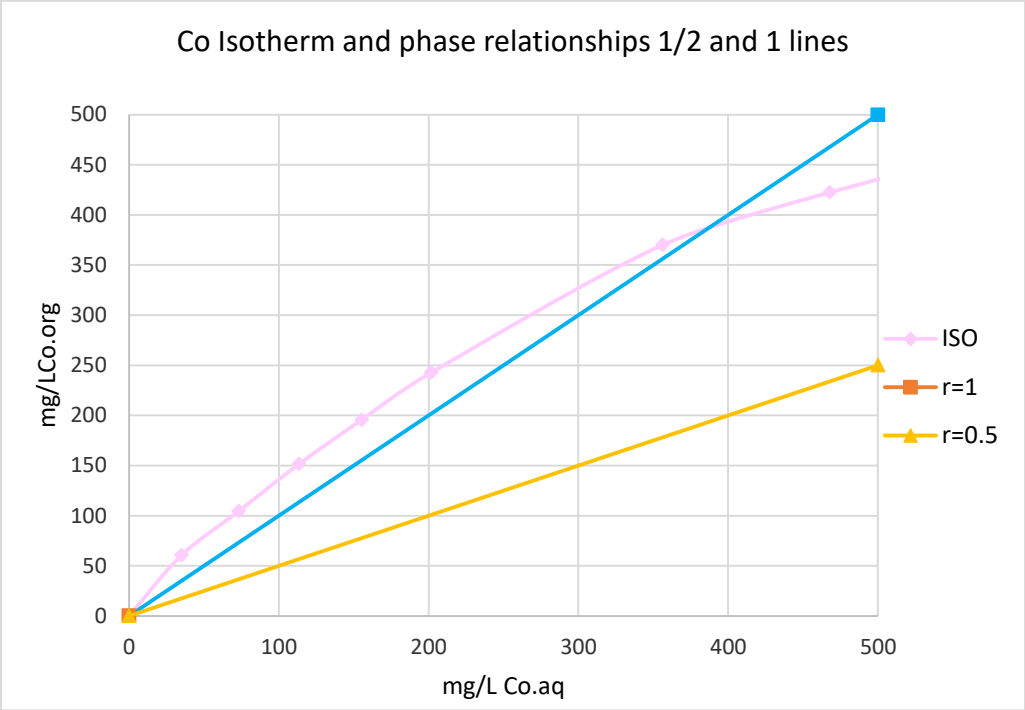


Fig 23: Co istothem + r=1 and r=0,5 lines

Having decided the operating line and plotted with the isotherm, it is just to start to draw stages from the operating line at 500ppm.

Since the nickel is barely moving to the aqueous phase, in comparison with cobalt, there is no need to invest time in the generation of a nickel isotherm.

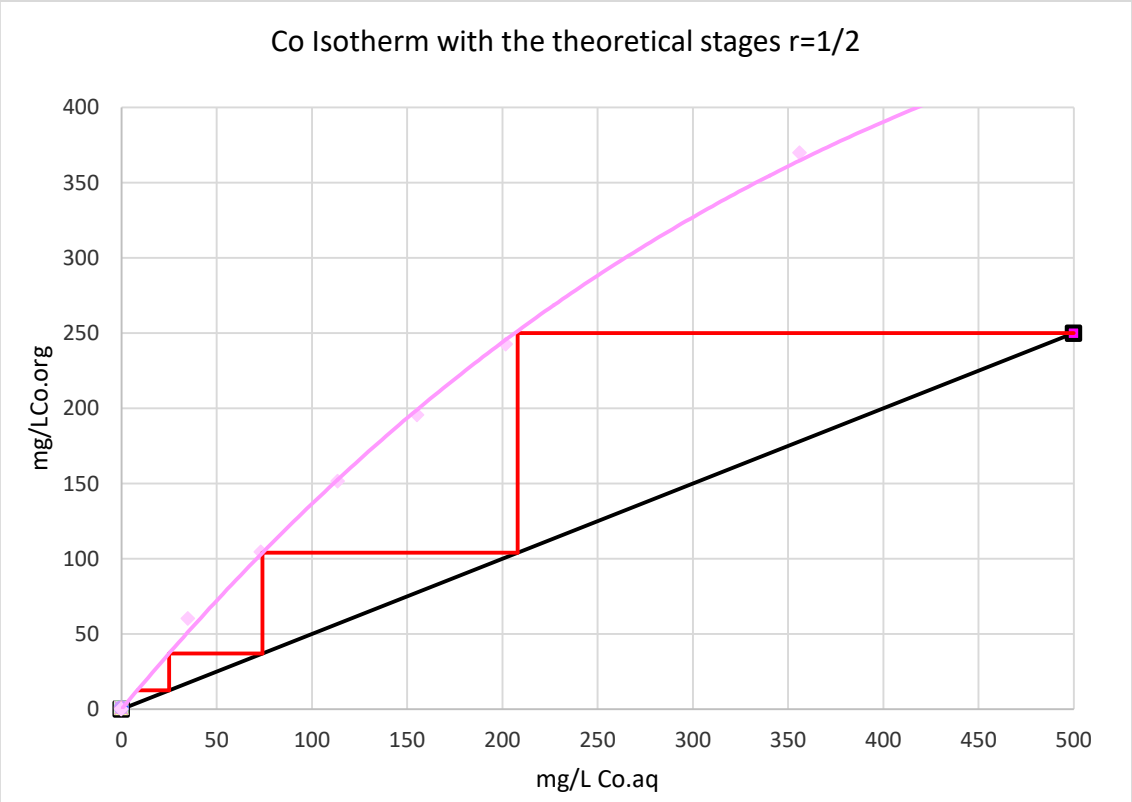


Fig 24: Theoretical number of stages

Having fixed the r=0,5 the 4 stages, where the equilibrium is reached in all of them, achieve a 4,25 ppm of cobalt which is a concentration good enough.

Due to its low value, it is not necessary to readjust the abscissa value because it could be considered that 4,25 and 0 are pretty close each other.

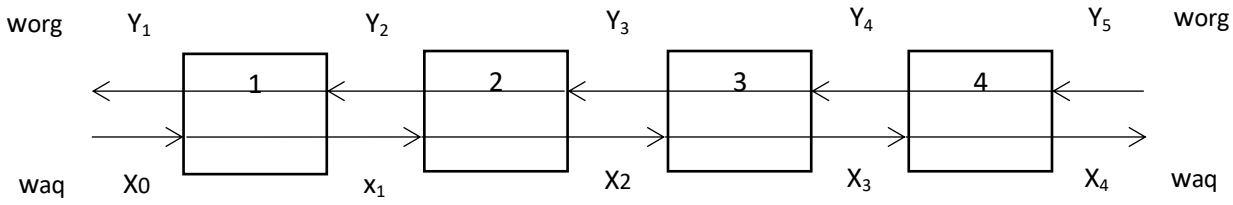


Fig 25: Theoretical countercurrent full scheme

On the other hand it is important to know that each set of 4 stages would correspond to a theoretical mixer-separator device. Here it is understood that these funnels in reality would work as a single operating unit with 4 equlibrium stages inside.

### 4.12.1. Countercurrent system stabilization

This part deals with the necessity of generating a method that could emulate a continous multistage process.

This method is based on how the metal retaining cargo stabilizes throughout various extractions. In fact, the 4 stages that represent the system have to pass through several cycles of extraction and reextraction in order to achieve this stability.

In the scheme below it is showed how the mass flows move through the funnels to recreate this desired behaviour.

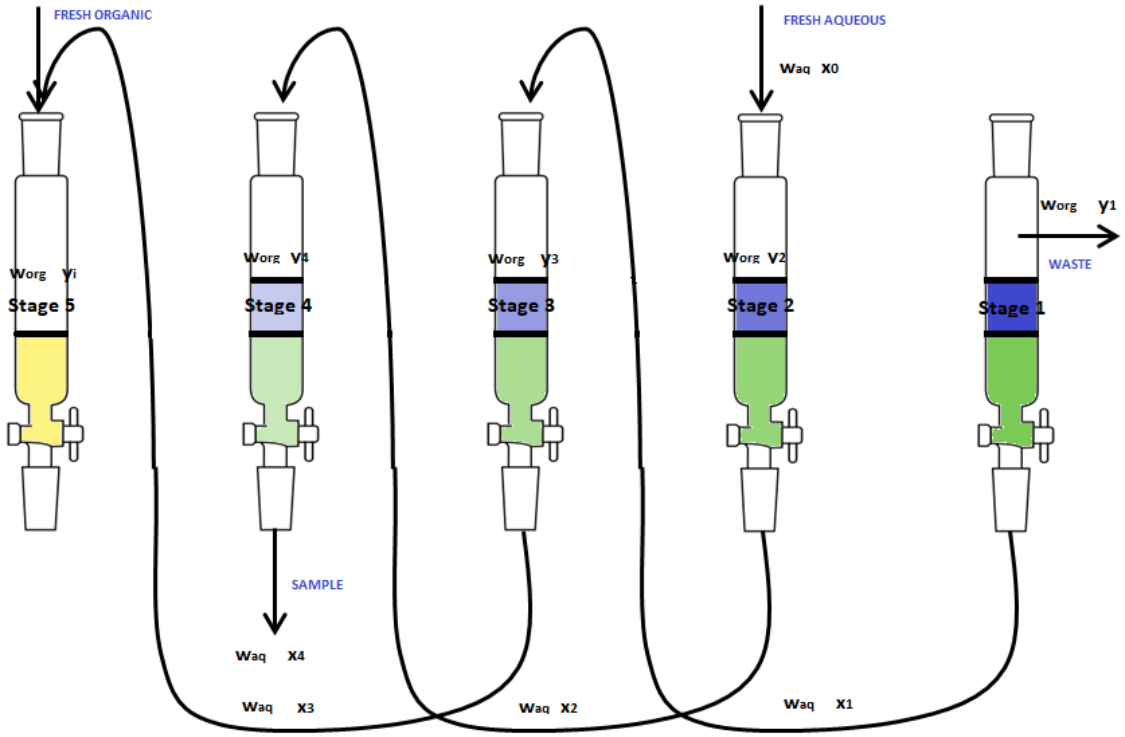


Fig 26: Scheme represented as funnels

As seen, the countercurrent process evolves whilst more samples are generated. Stripping may be done as well to see if mass balances are squared and permits to evaluate the results by two different ways, just in case.

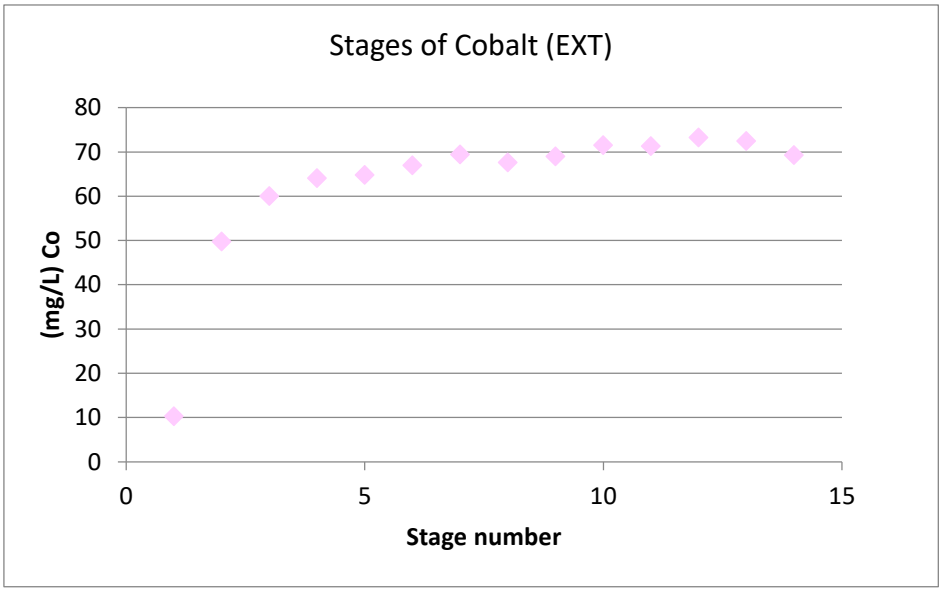


Fig 27: Cobalt stabilization

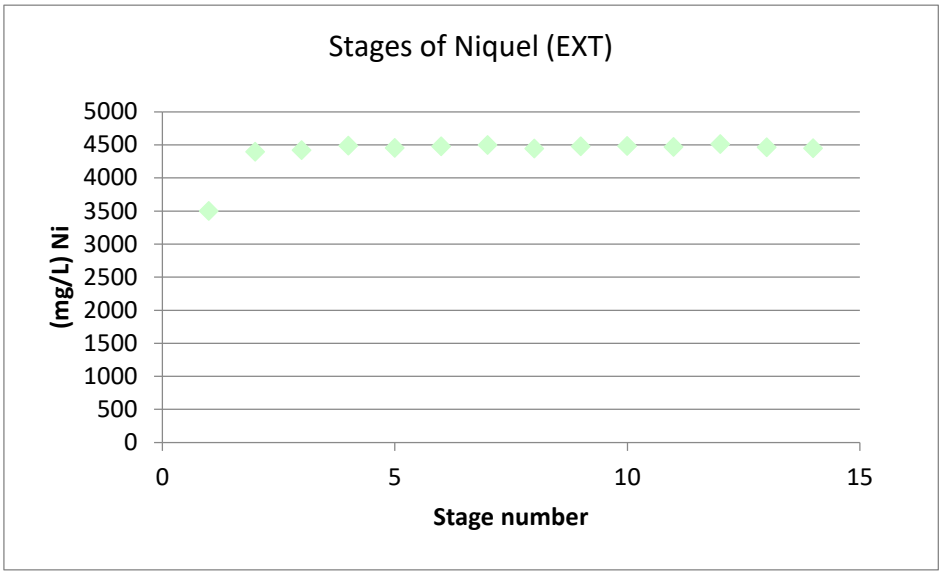


Fig 28: Nickel stabilization

It may be seen that that cobalt stabilizes at the seventh stage and nickel at the third. From this point, it is pointless to continue doing funnels because the system is stabilized.

Now, reached this point it is just separate the phases of the 4 last funnels and check if the concentrations results are close to the theoretical results obtained by McCabe-Thiele.

In this case it is quite hard to get a good correlation or have a low error because the organic phase has been slightly modified during this particular essay, adding a 5% (v/v) of decanol, to promote the phase separation which working at r=0.5 is quite hard. This is discussed later in seccion 4.12.3.

### 4.12.2. Results of the countercurrent process

Once the system is stabilized, the aqueous phases are separated to do the analysis.

In the following graph are plotted the points of experimental data together with the operating line and the isotherm. If the equilibrium is achieved, the experimental points should be near of the cobalt isotherm. Unfortunately it seems that there is something wrong with it because they are far from the curve.

Table 17: Cobalt concentrations at the different stages

| Co (experimentally obtained) | | | |
|---|---|---|---|
| Stage | [Co] aq (ppm) | Stage | [Co] org (ppm) |
| $X_0$ | 434,97 | - | - |
| $X_1$ | 217,48 | $Y_1$ | 202,34 |
| $X_2$ | 111,45 | $Y_2$ | 108,05 |
| $X_3$ | 54,28 | $Y_3$ | 52,23 |
| $X_4$ | 20,36 | $Y_4$ | 22,71 |
| - | - | $Y_i$ | 11,35 |

This may occur due to various facts. First, the isotherm is constructed from different initial concentrations of a single metal (whilst the other is fixed) and the countercurrent is carried out with just a solution which holds a fixed concentration of cobalt and nickel. Second, the organic solution used for this last experiment is not the same used to obtain the isotherm (as mentioned before) because working at r=0,5 the separation was quite difficult and it was unclear. Third, the time the funnels remained without separate both phases was quite long because there was a failure with the hardware and it was impossible to determine if the system was already stabilized.

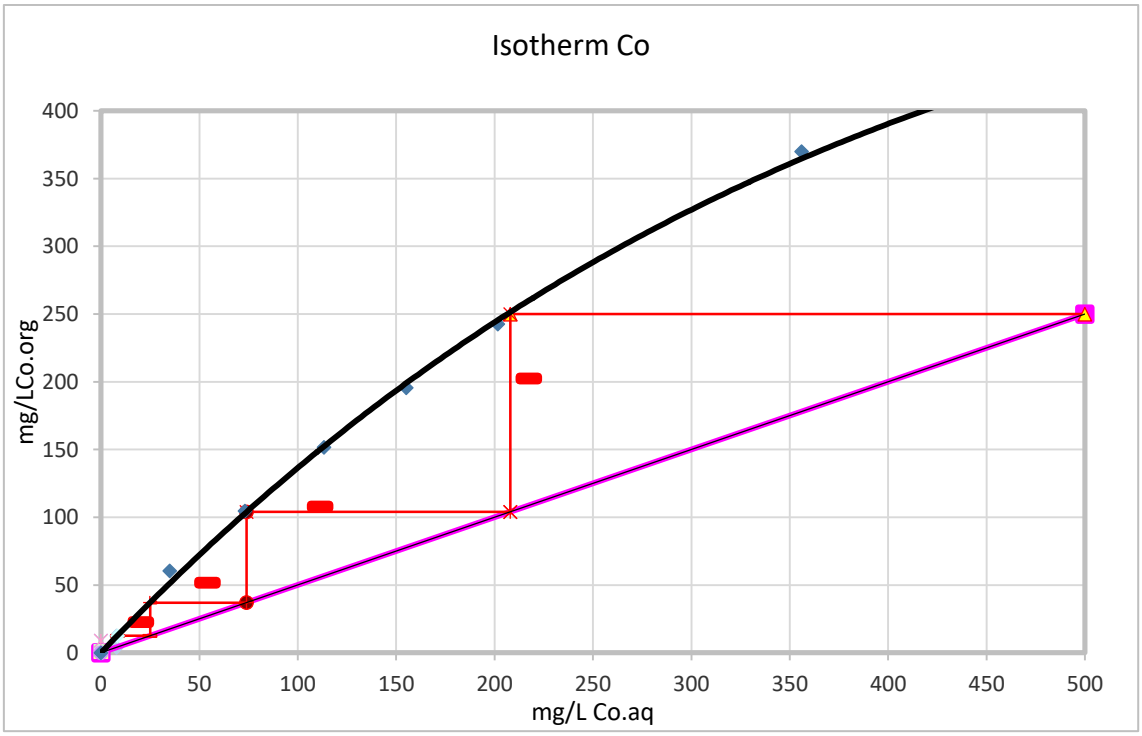


Fig 29: McCabe Thiele theoretical stages + experimental points

And below, the values of the thick red dots (experimental points).

Table 18: Countercurrent results

| Experimental stages (mg/L) | |
|---|---|
| 217,48 | 202,34 |
| 111,45 | 108,05 |
| 54,28 | 52,23 |
| 20,36 | 22,71 |

### 4.12.3. Conclusion

As it may be seen above, the results obtained experimentally does not correspond to the theoretical, but they are close enough. Maybe the addition of some 1-decanol during this experiment gave place to this difference. However, the extraction and separation have been a success because the cobalt has been reduced sharply, removing a big part from the initial aqueous phase.

Maybe, doing again the countercurrent experiment and separing the phases shortly after the extraction, to avoid oxidation and undesired effects, the results would be closer.

# 5. Model

## 5.2. Theoretical considerations

In this chapter, a new target is locked, that is to find a mathematical model that represents theoretically the extraction process that is being studied in this project. From this model is intended to predict the approximate behavior of a continuous process in countercurrent.

$$Me^{2+}{}_{free} + SO_4^{2-}{}_{free} + 2\overline{RH_2NA^-H^+} \leftrightarrow MeA_2 + \overline{(RH_2NA)_2SO_4} \quad (29)$$

And isolating the $K_{ext}$:

$$K_{ext} = \frac{|MeA_2| * \overline{|(RH_2NA)_2SO_4|}}{|Me^{2+}|_{free} * |SO_4^{2-}|_{free} * \left|\overline{RH_2NA^-H^+}\right|} \quad (30)$$

$|MeA_2|$ and $|(RH_2NA)_2SO_4|$. Are the equilibrium concentrations of the new species formed in the organic phase from the metal and the extracted sulphates

$|Me^{2+}|$ and $|SO_4^{2-}|$ as the oncentration in equilibrium of metal and free sulphate in the aqueous phase, which means that it is not forming any type of compound with the other can be written in a generic way although it will be applied to cobalt only

$|RH_2NAH|$is the concentration of the free extractant when passing the process is in equilibrium

A factor directly involved in the determination of the process constant is the formation of compounds between the metal and sulphates within the aqueous phase. These have to be considered because they take an important role in the system and also have to be considered in the mass balances.

In any case:

$$\beta 1_{Ni} = \frac{|NiSO_4|}{|Ni^{2+}|_{free} * |SO_4^{2-}|_{free}} \quad (31)$$

$$\beta 2_{Ni} = \frac{\left|Ni(SO_4)_2^{2-}\right|}{|Ni^{2+}|_{free} * |SO_4^{2-}|_{free}^2} \quad (32)$$

$$\beta 1_{Co} = \frac{|CoSO_4|}{|Co^{2+}|_{free} * |SO_4^{2-}|_{free}} \quad (33)$$

$|MeSO_4|$ and $|MeSO_4^{2-}|$Are the concentration of the new compound formed in equilibrium

$|Ni^{2+}|$ and $|Co^{2+}|$ Are the concentration of the free metal in the equilibrium aqueous phase

$|SO_4^{2-}|$ Is the concentration of free sulphate in the equilibrium aqueous phase

$|Me^{2+}|_{ini}$ as the metal concentration at the beginning.

$|Me^{2+}|_{AQ}$ as the overall metal concentration into the aqueous phase. This term gathers the the free metal plus the amount that is combined with sulphate.

$$|Me|_{aq} = |Me^{2+}|_{free} + \sum Me(SO_4)_x^{2-} \quad (34)$$

Where $Me(SO_4)^{2-}_X$ are the compunds formed by $Me^{2+}$ and $SO_4^{2-}$.

$|MeA_2|$ Concentration of the organometallic compound formed by the metal the extractant in the organic phase. This may be obtained as follows:

$$\overline{|MeA_2|} = |Me|_{org} = |Me|_{ini} - |Me|_{aq} \quad (35)$$

Concentration of total metal in the aqueous phase in this concentration is free metal and the one that is forming compounds with the sulphates.

$$|CoSO_4| = \beta 1_{Co} * |Co^{2+}|_{free} * \left|SO_4^{2-}\right|_{free} \quad (36)$$

Now, the compounds formed by the nickel with sulphate:

$$|NiSO_4| = \beta 1_{Ni} * |Ni^{2+}|_{free} * \left|SO_4^{2-}\right|_{free} \quad (37)$$

and

$$\left|Ni(SO_4)_2^{2-}\right| = \beta 2_{Ni} * |Ni^{2+}|_{free} * \left|SO_4^{2-}\right|^2_{free} \quad (38)$$

Now turning back to the metals. Their concentration in the aqueous phase is the sum o the free metal ($|Me|_{free}$) + the one that forms compounds. In the case of cobalt:

$$|Co|_{aq} = |Co^{2+}|_{free} + |CoSO_4| \quad (39)$$

which making the substitutions,

$$|Co|_{aq} = |Co^{2+}|_{free} + \beta 1_{Co} * |Co^{2+}|_{free} * \left|SO_4^{2-}\right|_{free} \quad (40)$$

and isolating:

$$|Co^{2+}|_{free} = \frac{|Co|_{aq}}{\beta 1_{Co} * |SO_4^{2-}|_{free} + 1} \quad (41)$$

Then, the same for nickel:

$$|Ni|_{aq} = |Ni^{2+}|_{free} + |NiSO_4| + \left|Ni(SO_4)_2^{2-}\right| \quad (42)$$

which making the substitutions:

$$|Ni|_{aq} = |Ni^{2+}|_{free} + \beta 1_{Ni} * |Ni^{2+}|_{free} * \left|SO_4^{2-}\right|_{free} + \beta 2_{Ni} * |Ni^{2+}|_{free} * \left|SO_4^{2-}\right|_{free}^2 \quad (43)$$

And isolating:

$$|Ni^{2+}|_{free} = \frac{|Ni|_{aq}}{1 + \beta 1_{Ni} * |SO_4^{2-}|_{free} + \beta 2_{Ni} * |SO_4^{2-}|_{free}^2} \quad (44)$$

Now, the sulphate is related with its several species as follows:

$$\left|SO_4^{2-}\right|_{free} = \left|SO_4^{2-}\right|_{ini} - \left|SO_4^{2-}\right|_{org} - \left|SO_4^{2-}\right|_{comp} \quad (45)$$

and developed for cobalt:

$$\left|SO_4^{2-}\right|_{free} = \left|SO_4^{2-}\right|_{ini} - \overline{|(RH_2NH^+)_2SO_4|} - |CoSO_4| \quad (46)$$

same to nickel:

$$\left|SO_4^{2-}\right|_{free} = \left|SO_4^{2-}\right|_{ini} - \overline{|(RH_2NH^+)_2SO_4|} - |NiSO_4| - 2 * \left|Ni(SO_4)_2^{2-}\right| \quad (47)$$

To know the concentration of the remaining extractant it is applied directly the stoichiometry:

$$|\overline{RH_2NAH}|_{free} = |\overline{RH_2NAH}|_{ini} - 2 * \overline{|MeA_2|} \quad (48)$$

same to the organic compound + sulphate:

$$\left|\overline{RH_2NH^+SO_4}\right| = 2 * |\overline{MeA_2}| \quad (49)$$

## 5.3. Cobalt stoichiometry results

By using a software called MEDUSA, the parameters of the especies that may appear in solution in a certain operationa pH are obtained, as shown in relations 24, 25, and 26.

According to these, the cobalt just uses one because the only specie formed with sulphate is $CoSO_4$ Instead of nickel, which has 2.

From these data, the stoichiometry, which initially was assumed as n=2 may be verified.

In the Annexes, the Table 37: Cobalt individually (stoichiometry) shows by linear approximation if this hypothesis was true by checking the slope of the line.

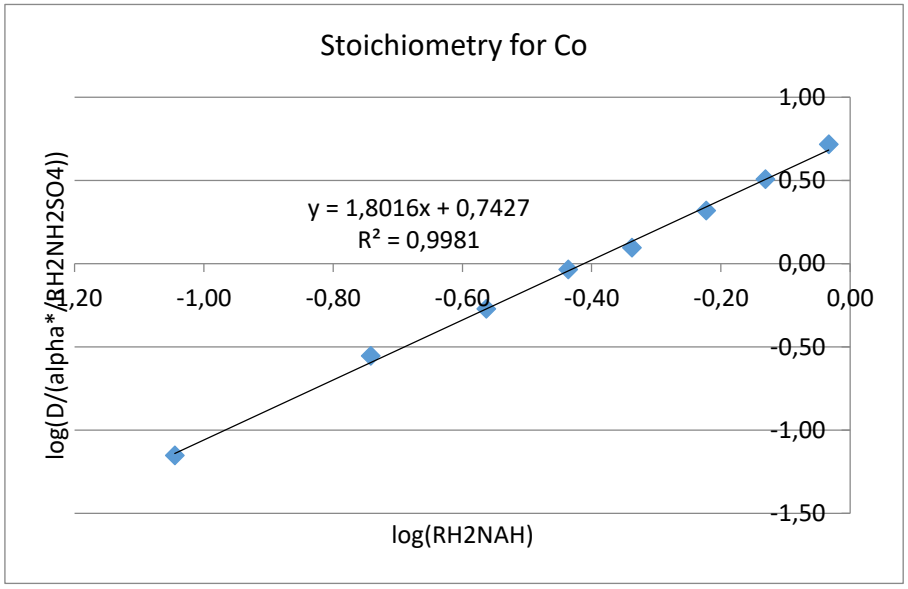


Fig 30: Stoichiometry for Co

By checking the slope, it may be seen that it is close enough to n=2 to consider it as correct.

So from the relation 29, which was expressed for a general metal ($Me^{2+}$), the eventual stoichiometry for cobalt is:

$$Co^{2+}{}_{free} + SO_4^{2-}{}_{free} + 2\overline{RH_2NA^-H^+} \leftrightarrow CoA_2 + \overline{(RH_2NA)_2SO_4} \quad (50)$$

To check the values in more detail , please go the the Excel Exp.Mod.xlsm (Model).

## 5.4. Nickel stoichiometry results

Now, following the previous steps and considerating relationships 24, 25 and 26, the stoichiometry of nickel may be obtained which was initially supposed as n=2 as well.

In the Annexes, the Table 38: Nickel individually (stoichiometry) shows by linear approximation if this hypothesis was true by checking the slope of the line.

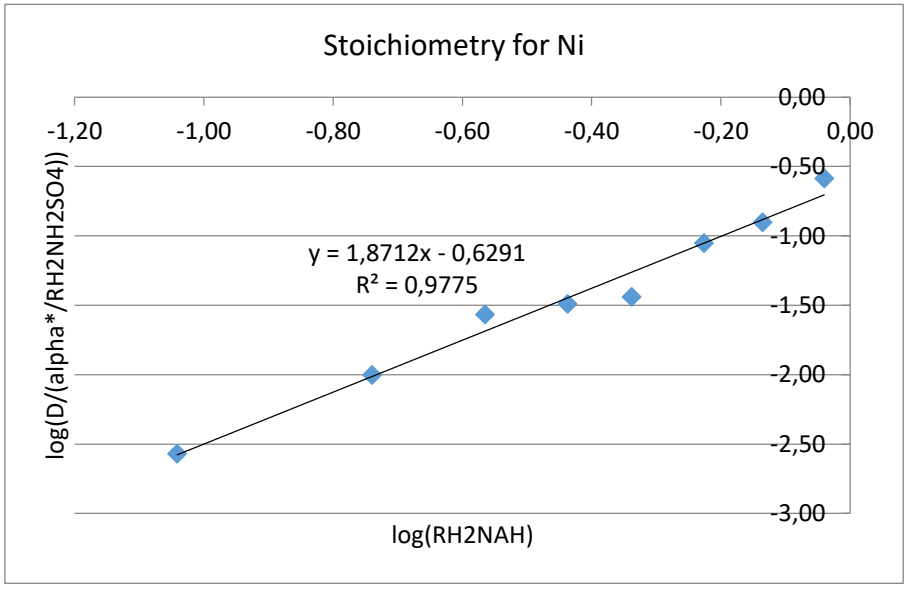


Fig 31: Stoichiometry for Ni

By checking the slope, it may be seen that it is close enough to n=2 to consider it as correct.

So from the relation 29, which was expressed for a general metal ($Me^{2+}$), the eventual stoichiometry for cobalt is:

$$Ni^{2+}{}_{free} + SO_4^{2-}{}_{free} + 2\overline{RH_2NA^-H^+} \leftrightarrow NiA_2 + \overline{(RH_2NA)_2SO_4} \quad (51)$$

## 5.5. Comparing the model with experimental data

From individual experimental data, available in the Excel document Exp.Mod.xlsm, may be generated a specific model for the current operational conditions.

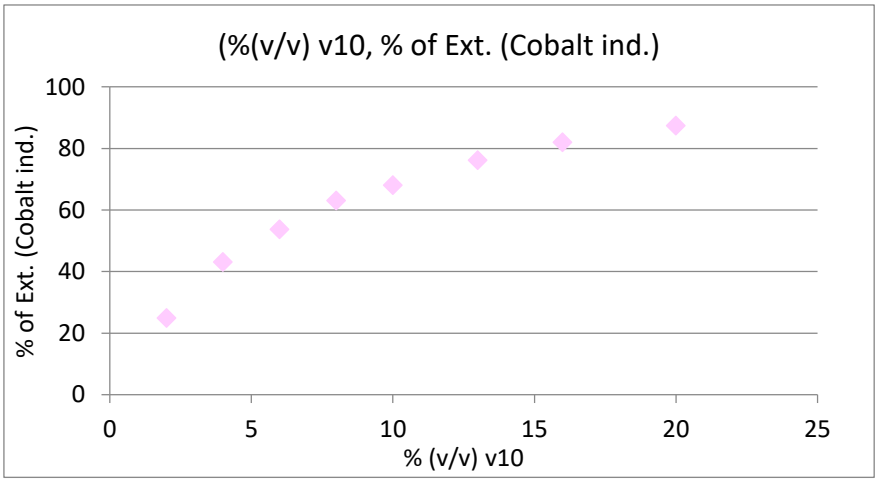


Fig 32: Experimental data for Cobal individually

It can be observed how it gives a higer ratio than the cobalt in mixture. Now, generating a model which bases on just one $K_{ext}$, a function can be constructed in order to find the minimum error from the quadratic error from both K's, experimental and theoretical.

$$Err = (K_{exp} - K_{theoretical})^2 \quad (52)$$

However to do this task, Excel's solver may lack of power if it is intended to apply the relation it altogether over all the experimental points.

Once obtained, in the current case $K_{ext}$ = 12,7 for cobalt, it may be used this constant to obtain one by one the different solutions. It may be approximated manually or giving a very good initialization.

Below it is shown the comparison between the data obtained and the K[1] of the extraction.

[1] As an additional hypothesis, it has been decided that nickel's comparison will be omitted. For more information in detail, please go and check Exp.Mod.xlsm "MODEL".

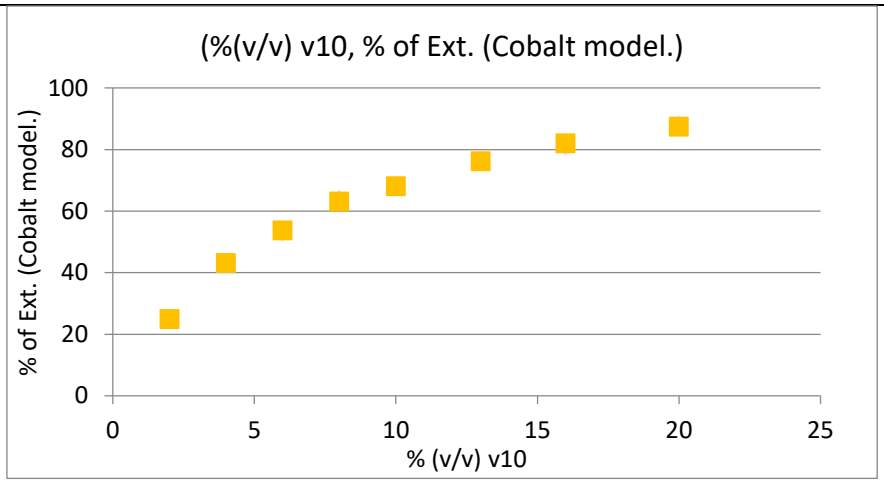


Fig 33: Comparison (Experimental vs Model)

A trend is almost completely eclipsed by the other. And also comparing it with data from the mixed cobalt:

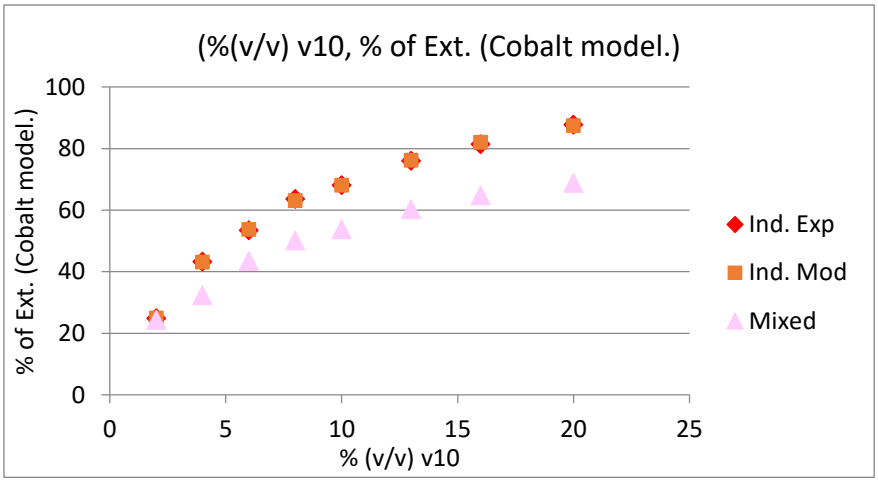


Fig 34: Comparison Experimentals vs model

Summary:

$K_{extCo}$: 12,727

$K_{extNi}$: 0,708

The value of cobalt is bigger than nickel, also its extraction ratio.

Also, highlight that it has been tried to program the same app by octave. The results are close to the obtained by Excel but there is a certain tendency to have a K quite unstable, maybe because it is a division and also an exponent, unlike the other equations. See more on the file “Octave”.

# 6. Environmental considerations and safety

In this chapter it is going to show several considerations that must be taken to do a project of this characteristics. Basically, it involves the usage of several reagents that generate a particular waste, so it must be treated correctly to avoid severe impact on the environament.

This aspects are limited and quantified under a set of standards that take in consideration the physical-chemical state, where the substances are dumped and if the waste departure is puntual or recurrent.

The same happens with the exposition to humans and operators, where several cases may occur, like punctual exposition, short or long-term injuries or the relation between toxicity and weight.

Before starting to discuss point by point, it is vital to have in mind the 2 concepts used to quantify the danger DNEL[1] and PNEC[2].

Obviously, the correct analysis would take lots of rules and standards but, to focus and do not go further, are discussed just the most relevant points to take awareness of which basic points should include a study of these features.

In both parts, it is very important to distinguish between the reagents nature and exposition. A good way to start is sort by physical state.

## 6.2. Environment

In this part, as mentioned, it is going to sort by 3 different physical states. All extra documentation, such as the maximum levels that may be dumped without any particular consideration, is attached in the Excel document called “Budget.Env.Safe.Prep.Glo.xlsm”.

[1] DNEL: It is de level of exposure that shall not be surpassed by humans to avoid any harm. The chemical manufacturers must attach this information in SDS.

[2] PNEC: The máximum concentration that ensures no harm for the environment. From this point the ecosystem would suffer several kinds of deterioration.

### 6.2.1. Solids

In this project there are not a huge variety of solids. Generally speaking it is just the glassware needed (that may be reused), the reagent containers, the disposable gloves and cleaning devices.

Depending on the nature of the reagents that have been in contact with these solids, they are dumped in the general container or in specials.

The glassware is conveniently separated and stored with “glass”, the reagent containers may be reused (not always) or dumped properly following the indications of the manufacturer. For disposable gloves, they all are dumped into a container that it is emptied by the lab technician following the standards and cleaning devices are dumped following the same principle. In case of doubt, the objects are stored safely, and the technician is warned to give them a correct treatment.

### 6.2.2. Liquids

Here it is the part that draws the attention mostly because most of the waste generated is in liquid state. Here, waste liquids are classified as “aqueous” and “organic” in first place.

#### 6.2.2.1. Aqueous

Secondly, the waste currents may be classified as concentrated or diluted according to the amount of metal contained. Mind that 5000 ppm is extremely higher than 100.

However, in the current project, those which held metal “tagged as Ni/Co” have been dumped in a single container.

Table 19: Some levels of PNEC in local freshwater

| Reagent | **mg/L (local freshwater)** |
|---|---|
| Acetone | **10,6** |
| Cobalt sulphate heptahydrate | **0,00051** |
| Decanol | **0,022** |
| Ethanol | **0,96** |
| Hydrochloric acid | **0,036** |
| Kerosene | **0,0066** |
| Sodium sulphate heptahydrate | **11,09** |
| Sulphuric acid | **0,0025** |

#### 6.2.2.2. Organic

In the case of organic, there is not distinction whether they contain metals or not. It was enabled a special container for organic waste.

### 6.2.3. Gases

In the current project this point is redundant because the amount of gases generated do not require special attention.

## 6.3. Safety

In this part, there are arranged some safety aspects to consider. They may be sorted according the physical state of the reagent that generates the risk.

### 6.3.1. Solids

Refering to solids, it is not a big deal to ensure a good protection wearing safety glasses and clothes and using disposable gloves.

The granulated reagents as the sulphates do not represent such danger following the previous instruction by may cause irritation. However, lots of glassware can be used in this experiment, just

handling them carefully (especially test tubes, made of fine glass susceptible to be broken) the operator health can be ensured.

### 6.3.2. Liquids

If the security devices are not enough to avoid the contact of the substances with the operator, it may be suffered:

- Corrosion: Especially by the action of strong acids as hydrochloric or sulfuric.
- Irritation: Especially by sulphates, acetone, kerosene and 1-decanol
- Burnings: Mostly with acetone, ethanol or kerosene.

### 6.3.3. Gases

It is very important to pay attention to gases because most of the reagents used may cause drowsiness and even fainting if the operator is not protected properly during a long period of time.

Even these products are not directly related to the process but the cleaning tasks such as acetone, for instance, they may produce strong breathing irritation that eventually might cause unconsciousness.

Following the instructions of the Safety Data Sheets[1] (SDS) and leaving the laboratory a few minutes when feel dizzy it is enough to prevent serious trouble.

[1] Some of the values that make reference to DNEL or PNEC are pretty hard to find or just “unavailable”. These are tagged in the document Budget.Env.Safe.Prep. Glo.xlsm. in “Safety and environment section”.

# 7. Project expenditure

In this chapter is created a sketch to estimate the amount of money needed to do the project. It gathers a set of considerations and hypothesis, and these are:

- It does include the reagents costs, the equipment (proportionally according to its usage) expenditure, services (water + electricity (just the related to consumption + IVA taxes)) and operator hiring costs.
- It does not include shipping costs, legal and non-direct costs. Also those that pay the university and may be underestimate.
- It does not gather any kind of isurance.
- Several values that are not available are estimated according to similar equipment and technicians advice.

## 7.2. Reagents expenditure

Table 20: Reagents expenditure according to manufacturers

| Row labels | Hexion | Labbox | Merck | Panreac | VidraFoc | (in blank) | Total general |
|---|---|---|---|---|---|---|---|
| Acetone | | 0,55 € | | | | | 0,55 € |
| Bidistillated water | | | | | | 9,00 € | 9,00 € |
| Cobalt standard for ICP | | | 3,73 € | | | | 3,73 € |
| Cobalt sulphate heptahydrate | | | 0,20 € | | | | 0,20 € |
| Decanol | | | | 1,14 € | | | 1,14 € |
| Ethanol | | 3,60 € | | | | | 3,60 € |
| Hydrochloric acid | | | | 1,92 € | | | 1,92 € |
| Kerosene | | | | | 9,92 € | | 9,92 € |
| Nickel standard for ICP | | | 3,73 € | | | | 3,73 € |
| Nickel sulphate hexahydrate | | | 6,10 € | | | | 6,10 € |
| Nitric acid | | | | 1,50 € | | | 1,50 € |
| Sodium bicarbonate | | | 1,47 € | | | | 1,47 € |
| Sodium sulphate heptahydrate | | | | | | 7,71 € | 7,71 € |
| Sulphuric acid | | | | 0,65 € | | | 0,65 € |
| Versatic acid 10 | 0,80 € | | | | | | 0,80 € |
| Total general | 0,80 € | 4,16 € | 15,22 € | 5,22 € | 9,92 € | 16,71 € | **52,02 €** |

## 7.3. Equipment costs

Table 21: Equipment expenditure according to manufacturers

| Row labels | Agilent technologies | Labbox | Tecnylab | Unknown | Total general |
|---|---|---|---|---|---|
| Agitator-Magnetic | | 24,40 € | | | 24,40 € |
| Agitator-Mechanic | | | | 25,00 € | 25,00 € |
| Beaker 100 mL | | 2,37 € | | | 2,37 € |
| Burette | | 1,61 € | | | 1,61 € |
| Cap-Flask | | 1,50 € | | | 1,50 € |
| Disposable gloves nitrile | | 6,44 € | | | 6,44 € |
| Generic gripper | | 3,88 € | | | 3,88 € |
| Glass flask | | 0,62 € | | | 0,62 € |
| MP-AES | 1.125,00 € | | | | 1.125,00 € |
| pH-meter | | 44,01 € | | | 44,01 € |
| Pipette tip (blue) | | 17,48 € | | | 17,48 € |
| Pipette tip (Macro 1) | | 17,48 € | | | 17,48 € |
| Pipette tip (Macro 2) | | | 10,97 € | | 10,97 € |
| Pipette tip (yellow) | | 17,48 € | | | 17,48 € |
| Spatule | | 0,46 € | | | 0,46 € |
| Support | | 2,09 € | | | 2,09 € |
| Volumetric flask 10 | | 3,17 € | | | 3,17 € |
| Volumetric flask 100 | | 4,06 € | | | 4,06 € |
| Volumetric flask 1000 | | 7,81 € | | | 7,81 € |
| Volumetric flask 25 | | 1,19 € | | | 1,19 € |

| | | | | | |
|---|---|---|---|---|---|
| Volumetric flask 250 | | 1,80 € | | | 1,80 € |
| Volumetric flask 5 | | 5,30 € | | | 5,30 € |
| Volumetric flask 50 | | 1,20 € | | | 1,20 € |
| Volumetric flask 500 | | 2,65 € | | | 2,65 € |
| Total general | 1.125,00 € | 166,97 € | 10,97 € | 25,00 € | **1.327,94 €** |

## 7.4. Services costs

Table 22: Overall cost of the services

| | |
|---|---|
| **Services (OVERALL)** | **16,84 €** |

### 7.4.1. Electricity expenditure

Table 23: Electricity expenditure

| | kWh | op. time | kW |
|---|---|---|---|
| Agitator | 1 | 20 | 20,00 |
| pH-meter | 0,01 | 40 | 0,40 |
| MP-AES 4100 | 1,632 | 30 | 48,96 |
| Auto sampler | 0,176 | 30 | 5,28 |
| Nitrogen generator 4007 | 0,04 | 30 | 1,20 |
| Air compressor | 1,1025 | 30 | 33,08 |
| Water heating | 0,4 | 15 | 6,00 |
| Wasching machine | 1 | 5 | 5,00 |
| Overall consumption | | | 119,92 kW |
| Cost of electricity | | | 13,79 € |
| Cost of electricity (with taxes +21%) | | | **16,69 €** |

### 7.4.2. Water service expenditure

Table 24: Water service expenditure

| | |
|---|---|
| Tap water consumption | 20,00L |
| Washing machine | 30,00L |
| Overall consumption | 50,00L |
| Price of water | 0,12 € |
| Price of water (with taxes +21%) | **0,15 €** |

## 7.5. Operator expenditure

Table 25: Operator expenditure

| OPERATOR | hours worked | tax contribution | Expenditure |
|---|---|---|---|
| Gross salary | 600 | 100,00% | 3600 |
| "SS.SS" | | 30,00% | 180 |
| "IRPF" | | 2,00% | 12 |
| | | Subtotal | **3.792,00 €** |

## 7.6. Overall expenditure

Here are gathered all the previous costs giving an idea of how much money is needed to develope this project.

Table 26: Overall expenditure

| | |
|---|---|
| REAGENTS EXPENDITURE | 52,02 € |
| EQUIPMENT EXPENDITURE | 1.327,94 € |
| SERVICES EXPENDITURE | 16,84 € |
| OPERATOR HIRING EXPENDITURE | 3.792,00 € |
| **OVERAL EXPENDITURE** | **5.188,79 €** |

The final expenditure value estimated is *five thousand one hundred and eighty-eight euros and seventynine cents*. Obviously, the real value will vary more or less depending on the hypotheses.

# 8. Conclusions

As a conclusion, point out that the process of liquid-liquid extraction which involves several variables to control and it requires a huge effort to synthesise the best extractant, has been understood.

From the 3 main points that represent this project in the best way (The extraction variables study, the generation of a countercurrent process simulation and a model elaboration), all 3 have been tried and, in general terms, the results are found within the range that was expected for them , according to literature.

Now, going point by point, all the important aspects are going to be discussed:

- The metal which is moving the most to the new phase is the cobalt, being the nickel the one that remains in the aqueous without moving. Comparing the data from the metals individually and mixed, nickel barly changes whilst cobalt increases a 20% its extraction if nickel is not found dissolved.
- Increaing the amount of amine, the extraction is higher but it does not mean that separation respond in the same way. Being the best concentration 13% (v/v) of amine (modifying just the amine and leaving stable the acid). However it has been chosen the theoretical equimolar point, witha 11,3% (v/v) of amine and 10% (v/v) of acid.
- The percentatge where the distribution ratio reaches its higher point is in 8% of v10, being PRIMENE 81-R fixed, saving the same relation.
- The pH measurement is considered a success because the ionic líquid synthesised does not generate too much $H^+$. Also, gives important clues about what has happened.
- The sulphate presence makes worse the extraction, also the presence of 1-decanol. However, by using the 1-decanol addition, it is more likely to get a quick separation for higher system volumes.
- The stoichiometries fixed as hipotheses n=2 have been a success. So the reaction evolves as imagined.
- The $K_{ext}$ obtained are 12,728 and 0,708, and the model responds correctly to the hyotheses so the difference between the mixed results and the model, are pretty the same, taking the consideration of the 20% more.
- It is created a countercurrent multistage process (4 stages), that reduces severly the concentration of cobalt into an aqueous phase. Then, all this cargo may be discharged on a new aqueous phase.

- Also, it has been appretiated, that the usage of a diluent in the organic phase gives a slightly better contact so the mass transfer is favoured.
- It has been quantified the amount of money necessary to do the project and it shows a result higher to 5000 €, so in is good to invest some time designing experiments instead of doing experiments without any control of results.
- The environmental aspects and safety considerations have been applied and fortunatelly there is not any problem to do this activity as long as all the waste goes to the especial containers and the operator has concious of the dangers of working in a laboratory, which involves the usage of certain standards.
- So, in conclusion, it could be said that all the points proposed have been achived in more or less degree, but the main target, that was to approach to selective liquid-liquid extraction techniques has been succesfully achieved.

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# ANNEXES

# A1. Experimental extraction data.

To see strippings and more, please adress to the attached document Exp.Mod.xlsm.

Table 27: Extraction results from Experiment 1 (EXP.1)

| | | (mg/L) Co | (mg/L) Ni | %Co | %Ni | Dco | Dni | Beta | Co | Ni |
|---|---|---|---|---|---|---|---|---|---|---|
| extr. | 9 | 183,02 | 4678,31 | 62,07 | 5,30 | 1,64 | 0,06 | **29,22** | 482,57 | 4702,97 |
| | 11 | 157,06 | 4577,39 | 67,45 | 7,35 | 2,07 | 0,08 | **26,14** | 478,83 | 4940,33 |
| | 12,5 | 124,04 | 4227,06 | 74,30 | 14,44 | 2,89 | 0,17 | **17,13** | | |
| | 13 | 118,77 | 4116,25 | 75,39 | 16,68 | 3,06 | 0,20 | **15,30** | | |
| | 15 | 108,64 | 3796,87 | 77,49 | 23,15 | 3,44 | 0,30 | **11,43** | | |

Table 28: Extraction results from Experiment 2 (EXP.2)

| | | (mg/L) Co | (mg/L) Ni | %Co | %Ni | Dco | Dni | Beta | Co | Ni |
|---|---|---|---|---|---|---|---|---|---|---|
| extr. | 0 | 487,798 | 3864,028 | 4,762 | 13,384 | 0,050 | 0,155 | 0,324 | 512,19 | 4870,1 |
| | 7 | 387,254 | 4011,526 | 24,393 | 10,078 | 0,323 | 0,112 | 2,879 | 494,97 | 4461,11 |
| | 8 | 355,538 | 4039,913 | 30,585 | 9,442 | 0,441 | 0,104 | 4,226 | | |
| | 9 | 301,457 | 3932,540 | 41,143 | 11,848 | 0,699 | 0,134 | 5,201 | | |
| | 10 | 243,965 | 3813,225 | 52,368 | 14,523 | 1,099 | 0,170 | 6,471 | | |
| | 11 | 226,198 | 3706,799 | 55,837 | 16,909 | 1,264 | 0,203 | 6,213 | | |
| | 12 | 198,184 | 3587,438 | 61,307 | 19,584 | 1,584 | 0,244 | 6,506 | | |
| | 13 | 173,795 | 3485,748 | 66,068 | 21,864 | 1,947 | 0,280 | 6,959 | | |

Table 29: Extraction results from Experiment 3 (EXP.3)

| | | (mg/L) Co | (mg/L) Ni | %Co | %Ni | Dco | Dni | Beta |
|---|---|---|---|---|---|---|---|---|
| | | 431,50 | 4159,36 | | | | | |
| | | | 4768,42 | | | | | |
| extr. | 2 | 326,65 | 4655,62 | 24,30 | 2,37 | 0,32 | 0,02 | 13,25 |
| | 4 | 292,20 | 4622,49 | 32,28 | 3,06 | 0,48 | 0,03 | 15,10 |
| | 6 | 244,10 | 4569,38 | 43,43 | 4,17 | 0,77 | 0,04 | 17,63 |
| | 8 | 215,46 | 4526,01 | 50,07 | 5,08 | 1,00 | 0,05 | 18,72 |
| | 10 | 199,76 | 4408,43 | 53,71 | 7,55 | 1,35 | 0,08 | 16,53 |
| | 13 | 171,28 | 4354,03 | 60,31 | 8,69 | 1,52 | 0,10 | 15,96 |
| | 16 | 152,12 | 4289,98 | 64,75 | 10,03 | 1,84 | 0,11 | 16,47 |
| | 20 | 134,45 | 4197,26 | 68,84 | 11,98 | 2,21 | 0,14 | 16,24 |

Table 30: Extraction results from Experiment 4 (EXP.4)

| | | (mg/L) Co | (mg/L) Ni | %Co | %Ni | Co(50) | Ni(50) | Ni(500) |
|---|---|---|---|---|---|---|---|---|
| extr. | 0,1 | 159,979 | 3432,805 | 67,656 | 18,309 | 494,619 | 4562,907 | 4202,157 |
| | 0,25 | 179,402 | 4126,849 | 61,724 | 12,185 | 468,705 | 4537,831 | 4699,494 |
| | 0,4 | 194,033 | 3418,775 | 57,584 | 11,720 | 457,448 | 4477,479 | 3872,641 |
| | 0,5 | 198,932 | 4070,028 | 54,312 | 8,715 | 435,410 | 4426,148 | 4458,584 |
| | 0,75 | 234,735 | 3532,657 | 45,613 | 7,548 | 431,602 | 4314,212 | 3821,066 |
| | 1 | 236,576 | 4362,735 | 41,441 | 5,200 | 403,999 | 4271,479 | 4602,028 |

Table 31: Extraction results from Experiment 5 (EXP.5)

| | | (mg/L) Co | (mg/L) Ni | %Co | %Ni361 |
|---|---|---|---|---|---|
| | 0 | 0 | | | |
| extr. | 100 | 34,968 | 4505,410 | 63,331 | 5,245 |
| | 200 | 73,271 | 4660,183 | 58,800 | 0,723 |
| | 300 | 113,497 | 4538,012 | 57,177 | 4,432 |
| | 400 | 155,256 | 4543,613 | 55,741 | 4,565 |
| | 500 | 201,729 | 4648,022 | 54,606 | 2,527 |
| | 800 | 356,119 | 4556,879 | 50,955 | 12,025 |
| | 1000 | 467,826 | 4670,206 | 47,446 | 1,276 |
| | 2000 | 1099,792 | 4569,286 | 38,071 | 3,954 |

Table 32: Extraction results from Experiment 5 (EXP.5)

| | | Co | Ni | %Co | %Ni |
|---|---|---|---|---|---|
| | 0 | 0 | | | |
| extr. | 1 | 10,236 | 3496,004 | 97,634 | 29,140 |
| | 2 | 13,712 | 4390,195 | 96,831 | 11,015 |
| | 3 | 15,065 | 4417,405 | 96,518 | 10,464 |
| | 4 | 17,029 | 4482,905 | 96,064 | 9,136 |
| | 5 | 18,491 | 4447,940 | 95,726 | 9,845 |
| | 6 | 19,724 | 4471,279 | 95,441 | 9,372 |
| | 7 | 20,643 | 4492,201 | 95,229 | 8,948 |
| | 8 | 19,899 | 4441,620 | 95,401 | 9,973 |
| | 9 | 20,191 | 4472,795 | 95,333 | 9,341 |
| | 10 | 19,812 | 4476,139 | 95,421 | 9,273 |
| | 11 | 20,160 | 4465,487 | 95,341 | 9,489 |
| | 12 | 20,562 | 4505,635 | 95,248 | 8,675 |
| | 13 | 20,690 | 4456,956 | 95,218 | 9,662 |

Table 33: Extraction results from Experiment 8 (EXP.8)

| | | Co | Ni | %Co | %Ni | (mg/L) ext Co | (mg/L)Ni ext |
|---|---|---|---|---|---|---|---|
| in1 | | 449,63 | 4667,73 | | | | |
| in2 | | 4667,73 | 4831,46 | | | | |
| E1.0% | 0 | 141,88 | 4286,63 | 68,445166 | | 307,75 | |
| E1.5% | 5 | 202,03 | 4372,45 | 55,0675 | | 247,6 | |
| E1.10% | 10 | 248,16 | 4361,77 | 44,807953 | | 201,47 | |
| E1.1:1 | | 206,42 | 4362,96 | 54,091142 | | | |
| E2.0% | 0 | 116,04 | 4337,38 | | 10,226308 | | 494,08 |
| E2.5% | 5 | 168,59 | 4434,3 | | 8,2202895 | | 397,16 |
| E2.10% | 10 | 228,53 | 4501,77 | | 6,8238172 | | 329,69 |
| E2.1:1 | | 179,45 | 4616,57 | | 4,4477239 | | |

Table 34: Extraction results from Experiment 9 (EXP.9)

| | | | | %Co | %Ni | Co(50) | Ni(50) | Ni(500) |
|---|---|---|---|---|---|---|---|---|
| extr. | 0,1 | 159,98 | 3432,80 | 67,66 | 18,31 | **494,62** | **4562,91** | **4202,16** |
| | 0,25 | 179,40 | 4126,85 | 61,72 | 12,19 | **468,71** | **4537,83** | **4699,49** |
| | 0,4 | 194,03 | 3418,78 | 57,58 | 11,72 | **457,45** | **4477,48** | **3872,64** |
| | 0,5 | 198,93 | 4070,03 | 54,31 | 8,71 | **435,41** | **4426,15** | **4458,58** |
| | 0,75 | 234,73 | 3532,66 | 45,61 | 7,55 | **431,60** | **4314,21** | **3821,07** |
| | 1 | 236,58 | 4362,74 | 41,44 | 5,20 | **404,00** | **4271,48** | **4602,03** |

Table 35: Extraction results from Experiment 10 (EXP.10)

| | | (mg/L) Co | | | |
|---|---|---|---|---|---|
| | | 463,32 | | | |
| | | | %Co | Dco | Co/NiCo |
| extr. | 2 | 336,06 | 27,47 | 0,38 | 0,91 |
| | 4 | 256,77 | 44,58 | 0,80 | 1,25 |
| | 6 | 209,49 | 54,78 | 1,21 | 1,18 |
| | 8 | 168,16 | 63,70 | 1,76 | 1,22 |
| | 10 | 143,98 | 68,92 | 1,35 | 1,24 |
| | 13 | 108,96 | 76,48 | 3,25 | 1,24 |
| | 16 | 82,07 | 82,29 | 4,65 | 1,25 |
| | 20 | 56,92 | 87,71 | 7,14 | 1,26 |

Table 36: Extraction results from Experiment 10 (EXP.10)

| | | (mg/L) Ni | | | |
|---|---|---|---|---|---|
| | | 4363,45 | | | |
| | | 4668,23 | %Ni | Dni | Ni/NiCo |
| extr. | 2 | 4610,23 | 1,24 | 0,01 | 0,53 |
| | 4 | 4522,29 | 3,13 | 0,03 | 1,02 |
| | 6 | 4402,25 | 5,70 | 0,06 | 1,58 |
| | 8 | 4367,15 | 6,45 | 0,07 | 1,27 |
| | 10 | 4098,53 | 8,31 | 0,14 | 1,10 |
| | 13 | 4155,26 | 10,99 | 0,12 | 1,26 |
| | 16 | 4104,78 | 12,07 | 0,14 | 1,20 |
| | 20 | 3875,77 | 16,98 | 0,20 | 1,42 |

Table 37: Cobalt individually (stoichiometry)

| Co sol | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| % Ext | Meini ppm | MeTaq ppm | MeTor ppm | D | $RH_2NAH$ | $RH2NH_2SO_4$ | log (RH2NAH) | log (D/a/RH2NH2SO4) |
| 2 | 463,32 | 348,08 | 115,24 | 0,33 | 0,09 | 0,00 | -1,05 | -1,15 |
| 4 | 463,32 | 263,75 | 199,57 | 0,76 | 0,18 | 0,00 | -0,74 | -0,56 |
| 6 | 463,32 | 214,24 | 249,08 | 1,16 | 0,27 | 0,00 | -0,56 | -0,27 |
| 8 | 463,32 | 171,09 | 292,23 | 1,71 | 0,37 | 0,00 | -0,44 | -0,04 |
| 10 | 463,32 | 147,74 | 315,58 | 2,14 | 0,46 | 0,01 | -0,34 | 0,09 |
| 13 | 463,32 | 110,43 | 352,89 | 3,20 | 0,60 | 0,01 | -0,22 | 0,32 |
| 16 | 463,32 | 83,18 | 380,14 | 4,57 | 0,74 | 0,01 | -0,13 | 0,51 |
| 20 | 463,32 | 58,20 | 405,12 | 6,96 | 0,93 | 0,01 | -0,03 | 0,72 |

Table 38: Nickel individually (stoichiometry)

| Ni sol | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| % Ext | Meini ppm | MeTaq ppm | MeTor ppm | D | $RH_2NAH$ | $RH2NH_2SO_4$ | log (RH2NAH) | log (D/a/RH2NH2SO4) |
| 2 | 4800,15 | 4709,05 | 91,10 | 0,02 | 0,09 | 0,00 | -1,04 | -2,57 |
| 4 | 4800,15 | 4626,64 | 173,51 | 0,04 | 0,18 | 0,00 | -0,74 | -2,00 |
| 6 | 4800,15 | 4516,75 | 283,40 | 0,06 | 0,27 | 0,00 | -0,56 | -1,57 |
| 8 | 4800,15 | 4491,30 | 308,85 | 0,07 | 0,37 | 0,01 | -0,44 | -1,49 |
| 10 | 4800,15 | 4473,92 | 326,23 | 0,07 | 0,46 | 0,01 | -0,34 | -1,44 |
| 13 | 4800,15 | 4299,41 | 500,74 | 0,12 | 0,59 | 0,01 | -0,23 | -1,05 |
| 16 | 4800,15 | 4211,51 | 588,64 | 0,14 | 0,73 | 0,01 | -0,14 | -0,90 |
| 20 | 4800,15 | 3975,35 | 824,80 | 0,21 | 0,91 | 0,01 | -0,04 | -0,59 |

# A2. Octave function and program

## Function

```
function F = funcion(x,y)

    %Incognitas
    c = x(1);
    d = x(2);
    e = x(3);
    f = x(4);
    g = x(5);
    ii =x(6);
    k = x(7);
    m = x(8);

    %Variables
    a = y(1);
    b = y(2);
    h = y(3);
    jj = y(4);
    l = y(5);
    %m = y(6);

%k = 0.5;
    F(1) = a - b -c;
    F(2) = f - b./(1+jj*k);
```

```
F(3) = d - jj*f*k;

F(4) =  d + k + e - l;

%F(4) = 0;

F(5) = m - e;

F(6) = ii - h +2*e;

F(7) = c - e;

%F(8) = g - e*m./(f*k*ii^2);

%F(8) = g - e*m./(f*k*ii);

F(8) =( g - e*m./(f*k*ii));


end
```

## Program

The parameters are introduced

```
num = 8; %Number of parameters

%a = [400];
a = 0.00786*ones(1,8);
b = [5.91 4.48 3.64 2.90 2.55 1.87 1.41 0.99]*10^(-3);
h = [0.09 0.19 0.28 0.38 0.47 0.61 0.75 0.94];
jj = 218*ones(1,8);
l = 0.5*ones(1,8);
%m = [16 17 18];

%a = rand(num,1);
%b =  rand(num,1);
%h =  rand(num,1);
%jj =  rand(num,1);
%l =  rand(num,1);
%m =  rand(num,1);



Cv = zeros(num,1);
Dv = Cv;
Ev = Cv;
Fv = Cv;
Gv = Cv;
IIv = Cv;
Kv = Cv;
Mv = Cv;

acc_vec = [];

for ind = [1:num]
        y = [a(ind) b(ind) h(ind) jj(ind) l(ind)];
        fun = @(x)funcion(x,y);
        x0 = rand(1,8);
        x0(5) = 1;
        %x0(1) = 6*10^-5; %c
        %x0(2) = 0.007; %d
        %x0(3) = 6*10^-5; %e
        %x0(4) = 5*10^-5; %f
        %x0(5) = 1;
        %x0(6) = 0.3; %ii
        %x0(7) = 0.5; %k
```

```
        %x0(8) = 5*10^-4; %m
        xs = fsolve(fun,x0);
        disp('miro la c')
        xs(1)
        disp('miro la e')
        xs(3)
        disp('miro la comp 7')
        resu = funcion(xs,y);
        %resu(7)
        resu
%       pause
        acc = sum(abs(resu));
        acc_vec = [acc_vec acc];
        Cv(ind) = xs(1);
        Dv(ind) = xs(2);
        Ev(ind) = xs(3);
        Fv(ind) = xs(4);
        Gv(ind) = xs(5);
        IIv(ind) = xs(6);
        Kv(ind) = xs(7);
        Mv(ind) = xs(8);
end

acc_vec

Cv
Dv
Ev
Fv
Gv
IIv
Kv
Mv
```

## Results

function

$|Co|_{org}v$ =

0.0019500

0.0033800

0.0042200

0.0049600

0.0053100

0.0059900

0.0064500

0.0068700

$|CoSO_4|v$ =

0.0062521

0.0051569

0.0052215

0.0042942

0.0040643

0.0022978

0.0033057

0.0037144

$|CoA_2|v$ =

0.0019500

0.0033800

0.0042200

0.0049600

0.0053100

0.0059900

0.0064500

0.0068700

$|Co^{2+}|_{free}v$ =

1.4024e-04

9.8730e-05

1.0219e-04

6.8586e-05

6.0069e-05

2.8144e-05

4.2618e-05

4.1243e-05

(K)v =

7.3871

6.9690

4.7638

5.2911

4.4939

7.2329

3.6304

2.6903

$|RH_2NHA|_{ini}$v =

0.086100

0.183240

0.271560

0.370080

0.459380

0.598020

0.737100

0.926260

$|SO_4|^{2-}v$ =

0.49511

0.49450

0.49603

0.49497

0.49496

0.49287

0.49490

0.49578

$|(RH2NH)_2SO_4|v$ =

0.0039000

0.0067600

0.0084400

0.0099200

0.0106200

0.0119800

0.0129000

0.0137400

# A3. Mp aes 4100

It is a measuring device developed by Agilent Technologies which is the first commertially available mp plasma on the market. It measures much more accurately than Flame Atomic Absortion (FAA) devices. It runs on air using a nitrogen generator and it doesn't require any water to operate.

It has a higher performance compared with a flame atomic absortion also low cost of ownership, improved safety considerations and easy to operate.

Inside the MP there are an industrial magnetron of 2.5GHz and a wave guide. The energy is transferred to the waveguide assembly, which focuses the energy created in axial magnetic and radial electrical fields. By focusing in containing the energy around the torch, plasma is created.

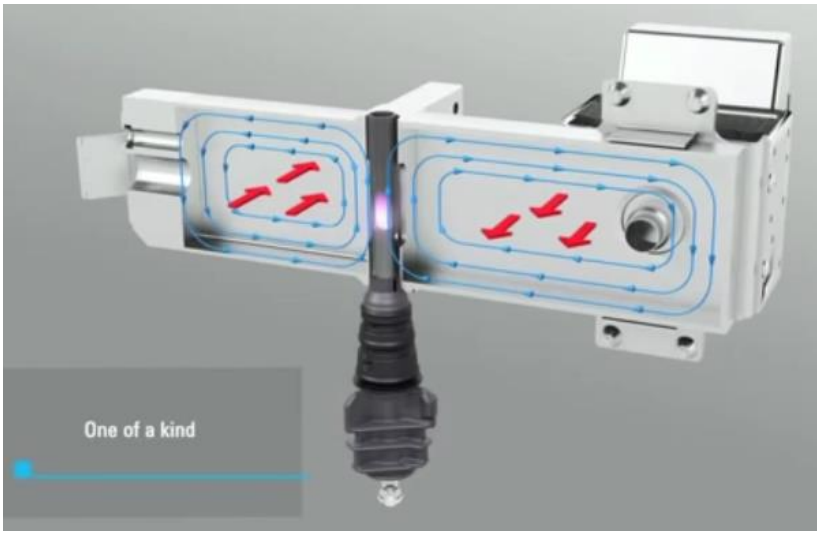


Fig 35: Torch creating the flame

It runs on air, which comes from a nitrogen generation (Agilent Technologies 4107 Nitrogen Generator) that eliminates ongoing gases and supplies infinite nitrogen. This is necessary because it is very important to have isolated nitrogen to run the machine which forms plasma on a conventional torch producing high-intensity emission lines.

Close to the torch, there is an aerosol that enters the sample. This, as long as is approaching, is dried, decomposed and atomized it returns to lower energy states, emitting the particular wave lines for each element.

This wave lines enters an internal optical system, where the light is decomposed and a fast-scan monochrometer transmits the wave line to an accurate CCD detector and measured according to the MP's configuration.

# A4. MP-AES quick guide

Previous actions

External hardware

First of all, the MP-AES operator has to ensure that compressed dry air arrives to the attached devices so, a compressor is turned on to do this task. Gathering air from the environment at high pressure there is a moisture purge and after all this flow goes to the air dryer in order to remove the remaining moisture.

The following device is the nitrogen generator (4107) which generates the demanding gas for the operation. It is turned on once the levels of moisture displayed by the air dryer are minimum.

Then, an extraction hood is activated to take all the gases produced in the measuring and dumped outside.

At this point, the tubes are fixed and the MP-AES and the sample injector turned on.

Having reached this point, all the hardware is operative. From now on, it is just to check that the torch, the tubes or the level of cleaning solution are correct.

Software setting

First of all, the MP Expert, which is the specific software for this kind of devices is run. This opens a welcome interface with 3 options. “Open” an existent document, “New from” an existent document or just a “New” one to start an analysis.


Fig 36: MP Expert Home Interface

After generating a new file, an interface with the periodic table appears. Here, it is just selecting the elements which are going to be analysed. There is also an additional consideration if the elements are measured in frequencies were interferences may occur, that is to select another frequency of the list which may also measure the concentration of a certain specie, but at the same time, generating the minimum interferences with the rest.

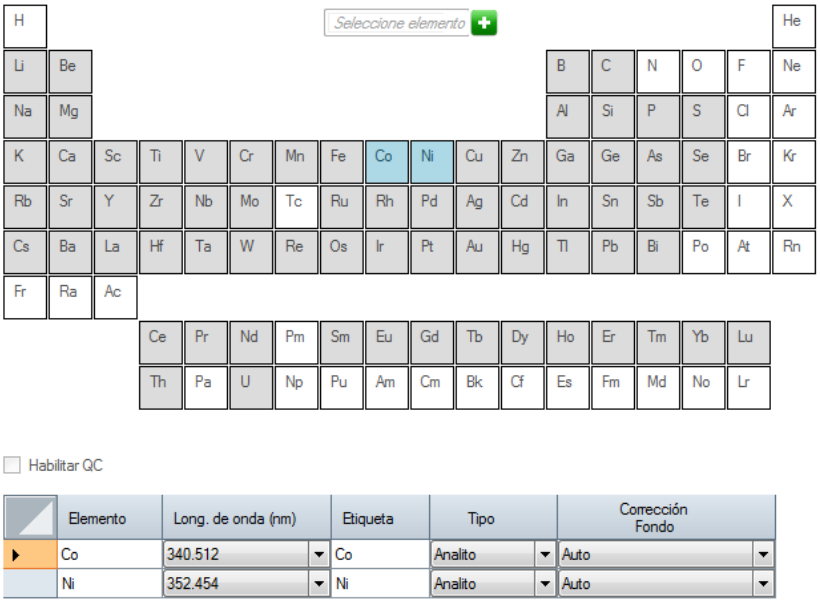


Fig 37: Element selection Interface

Fortunately, the software includes this function so, if there is any doubt, the frequencies that may give place to interferences are shown in red in the window below.

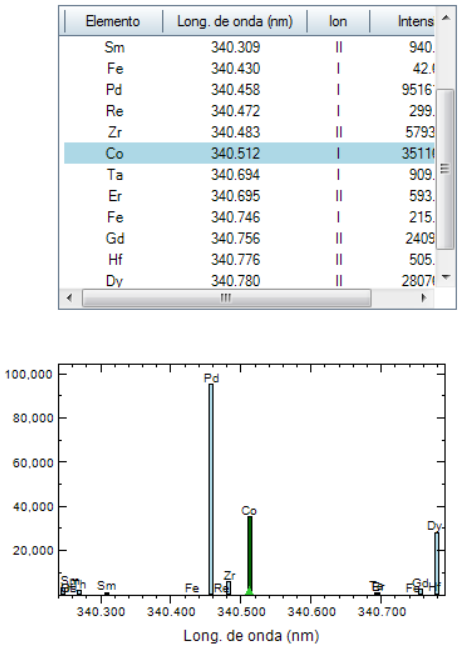


Fig 38: Wave length adjustments

Once the elements and the wave lengths are set, it is necessary to stablish the operation of the hardware. The configuration will vary according to the sample conditions but in the current situation, for instance, with two metals and some sulphate, the preset conditions are barely changed.

Normally, it will be selected a configuration that includes 3 replicas, 30 seconds of cleaning and 20 seconds of stabilization with 5 to 10 seconds of measuring.

Additionally, if it has not been doing yet, it is essential to check if the software recognizes any anomaly in the MP-AES internal hardware. This is shown in a tab called “instrument”.

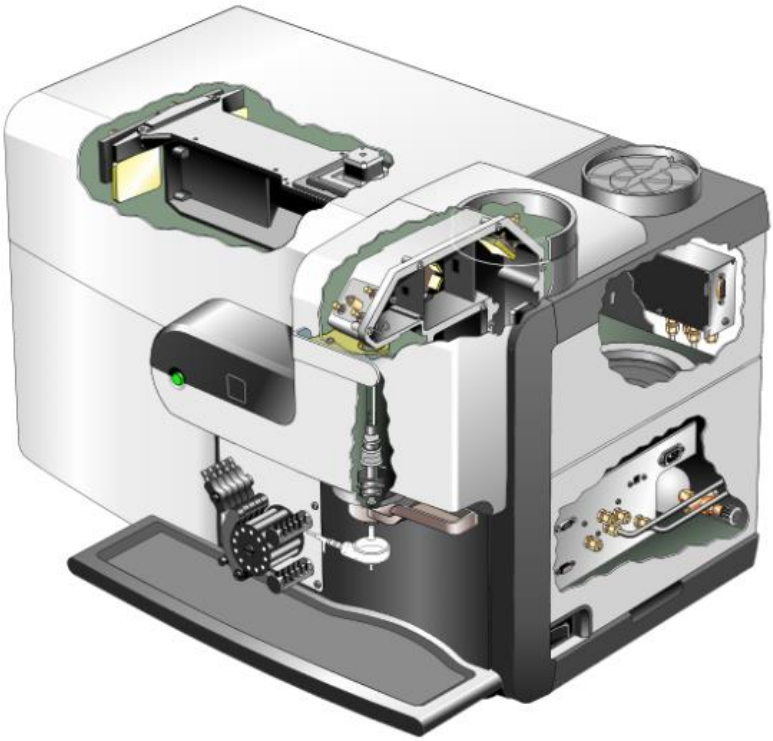

Fig 39: MP-AES Internal systems scheme

There, it appears the previous image. In case all the systems work correctly the image will be displayed as the figure shown, otherwise there will be some warning messages and the subsystem affected will be slightly colored in red.

At this point, it is just tag the samples, select the order chosen during the analysis, define the standards and set other operational conditions.

| Gradilla:tubo | Etiqueta de disolución | Tipo de disolución | Peso (g) | Volumen (ml) | Dilución |
|---|---|---|---|---|---|
| 1:1 | inicial1 | Muestra | 1.0 | 1.0 | 50.0 |
| 1:2 | inicial2 | Muestra | 1.0 | 1.0 | 500.0 |
| 1:3 | E1.AIS.0% | Muestra | 1.0 | 1.0 | 50.0 |
| 1:4 | E1.AIS.7% | Muestra | 1.0 | 1.0 | 50.0 |
| 1:5 | E1.AIS.8% | Muestra | 1.0 | 1.0 | 50.0 |
| 1:6 | E1.AIS.9% | Muestra | 1.0 | 1.0 | 50.0 |
| 1:7 | E1.AIS.10% | Muestra | 1.0 | 1.0 | 50.0 |
| 1:8 | E1.AIS.11% | Muestra | 1.0 | 1.0 | 50.0 |
| 1:9 | E1.AIS.12% | Muestra | 1.0 | 1.0 | 50.0 |
| 1:10 | E1.AIS.13% | Muestra | 1.0 | 1.0 | 50.0 |
| 1:11 | E2.AIS.0% | Muestra | 1.0 | 1.0 | 500.0 |
| 1:12 | E2.AIS.7% | Muestra | 1.0 | 1.0 | 500.0 |
| 1:13 | E2.AIS.8% | Muestra | 1.0 | 1.0 | 500.0 |

Fig 40: Fixing the dilution parameters

For the standards it is just define the range of standards and fix some parameters.

Then it is just prepare the hardware, turning on the pump whilst the injector takes acid nitric, wait 5 minutes until the equipment is stabilized and has the operating nítric acid solution within, turn on the plasma another 5-10 minutes whilst the inyector still takes acid and start the analysis.

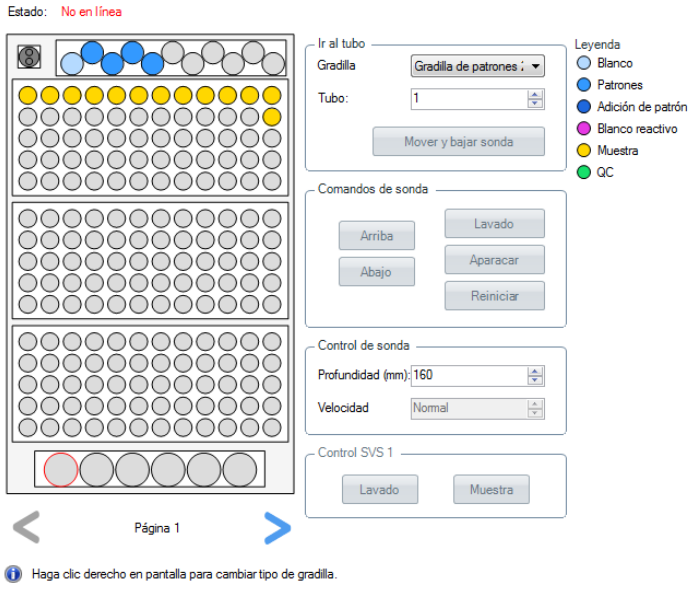


Fig 41: Injector autosampler scheme

## Measuring

Once the analysis has started, it is convenient to have an operator controlling regularly the operation of the device. In case that one of the tubes fail in a part of the connections, sue to a leak, for instance, the system could not receive the necessary flux of nitric acid and eventually the torch might break.